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(54) **TABLETTES DE DETERGENT A LESSIVE ET DE PRODUIT DE NETTOYAGE**

(54) **LAUNDRY DETERGENT AND CLEANING PRODUCT TABLETS**

(57) By impressing particulate ingredients into a cavity in a precompressed tablet it is possible to improve the adhesion of the filling, rule out temperature exposure of the ingredients, and minimize the apparatus required.

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Abstract:

By impressing particulate ingredients into a cavity in a precompressed tablet it is possible to improve the adhesion of the filling, rule out temperature exposure of the ingredients, and minimize the apparatus required.

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"Laundry detergent and cleaning product tablets"

Field of the Invention

The present invention relates to laundry detergent and cleaning product tablets, to processes for producing them and to their use.

Background of the Invention

Laundry detergent and cleaning product tablets have been widely described in the prior art and are enjoying increasing popularity among users owing to the ease of dosing. Tableted cleaning products have a number of advantages over their powder-form counterparts: They are easier to dose and to handle, and have storage and transport advantages owing to their compact structure. Consequently, there exists an extremely broad prior art relating to laundry detergent and cleaning product tablets, which is also reflected in an extensive patent literature. At an early stage, the developers of products in tablet form hit upon the idea of using tablet regions of different composition to release certain ingredients only under defined conditions in the course of washing or cleaning in order to improve the end result. Tablets which have become established in this context are not only the core/sheath tablets and ring/core tablets, which are sufficiently well known from pharmacy, but also, in particular, multilayer tablets, which are nowadays available for many segments of washing and cleaning or of hygiene. Visual differentiation of the products is also becoming increasingly important, so that single-phase and single-color tablets in the field of washing and cleaning have been largely displaced by multiphase tablets. Common current market forms include two-layer tablets having a white and a colored phase or having two differently colored layers. In addition, there exist inlay tablets, ring-core tablets, laminated tablets, etc., whose importance at present is fairly minor.

Multiphase cleaning tablets for the WC are described, for example, in **EP 055 100** (Jeyes Group). This document discloses toilet cleaning blocks comprising a shaped body, consisting of a slow-dissolving cleaning product composition, into which a bleach tablet has been embedded. At the same time, this document discloses the very wide variety of design forms of multiphase tablets. In accordance with the teaching of this document, the tablets are produced either by inserting a compressed bleach tablet into a mold and casting the cleaning product composition around this tablet, or by casting part of the cleaning product composition into the mold, followed by the insertion of the compressed bleach tablet and, possibly, subsequent overcasting with further cleaning product composition.

In addition, **EP 481 547** (Unilever) describes multiphase cleaning product tablets which are intended for use for machine dishwashing. These tablets have the form of core/sheath tablets and are produced by stepwise compression of the constituents: first of all, a bleach composition is compressed to form a tablet, which is placed in a die which is half-filled with a polymer composition, this die then being filled up with further polymer composition and compressed to form a bleach tablet provided with a polymer sheath. The process is subsequently repeated with an alkaline cleaning product composition, so as to give a three-phase tablet. This document says nothing about enzymes and enzyme performance.

Another route to producing visually differentiated laundry detergent and cleaning product tablets is described in International Patent Applications **WO99/06522, WO99/27063 and WO99/27063** (Procter & Gamble). According to the teaching of these documents, a tablet is prepared which has a cavity that is filled

with a solidifying melt. Alternatively, a powder is introduced and is fixed in the cavity by means of a coating layer. A common feature of all three applications is that the region filling out the cavity should not be compressed, since the intention is in this way to deal gently with "pressure-sensitive" ingredients.

The route described in the prior art of preparing melts into which tablets are inserted or which are cast into tablets involves a thermal load on the ingredients in the melts. In addition, the exact metering of media liquid to pastelike in consistency, and the subsequent cooling, necessitate great technical effort, which depending on the composition of the melt is in some cases destroyed by shrinkage on cooling and the detachment of the filling that this causes. The filling of cavities with powder-form ingredients, and fixing by means of coating, is likewise complex and hampered by similar stability problems.

The conventional tableting of multilayer tablets likewise reaches its limits in the field of laundry detergent and cleaning product tablets if one layer is intended to comprise only a small fraction of the total tablet. Below a certain layer thickness, compression of a layer adhering to the remainder of the tablet becomes increasingly difficult.

It is an object of the present invention, then, to provide tablets in which even temperature-sensitive ingredients may be accommodated in delimited regions, without any restrictions on the size of the delimited region in relation to the total tablet. At the same time, moreover, firstly there ought to be visual differentiation from conventional two-layer tablets and secondly the production of the tablets ought to function reliably without great technical effort and

even in mass production without the tablets suffering from stability drawbacks and without the fear of dosing inaccuracies.

Summary of the Invention

It has now been found that the abovementioned disadvantages are avoided if particulate ingredients are pressed into a cavity of a precompressed tablet. In this way, the adhesion of the filling is improved, the temperature load on the ingredients is avoided, and the apparatus required is minimized.

The invention provides laundry detergent and cleaning product tablets comprising

a) a compressed part (base tablet), which has at least one depression, and

b) at least one further compressed part which is present impressed into said depression(s) in the base tablet.

Detailed Description of the Invention

The compressed part a) of the laundry detergent and cleaning product tablets of the invention is described using the term "base tablet" and in the context of the present invention distinguishes the tablet produced by conventional tableting operations which has a depression. In preferred embodiments of the present invention, the base tablet is produced first of all and the further pressed part is applied or introduced onto or into this base tablet in a further operation. The resulting product is subsequently referred to by the generic term "tablet".

The base tablet may take on any geometric form whatsoever, with particular preference being given to concave, convex, biconcave, biconvex, cubic, tetragonal, orthorhombic, cylindrical, spherical, cylinder-segmentlike, discoid, tetrahedral, dodecahedral, octahedral, conical, pyramidal, ellipsoid, pentagon-, heptagon- and octagon-prismatic,

and rhombohedral forms. It is also possible to realize completely irregular outlines such as arrow or animal forms, trees, clouds, etc. If the base tablet has corners and edges, these are preferably rounded off. As additional visual differentiation, an embodiment having rounded corners and beveled (chamfered) edges is preferred.

The form of the depression may also be chosen freely, preference being given to tablets in which at least one depression may take on a concave, convex, cubic, tetragonal, orthorhombic, cylindrical, spherical, cylinder-segmentlike, discoid, tetrahedral, dodecahedral, octahedral, conical, pyramidal, ellipsoid, pentagon-, heptagon- and octagon-prismatic, or rhombohedral form. It is also possible to realize entirely irregular depression forms, such as arrow or animal forms, trees, clouds, etc. As with the base tablets, depressions having rounded corners and edges or having rounded corners and chamfered edges are preferred. Particular preference is given to depression forms as described in the earlier German Patent Application **DE 198 22 973.9** (Henkel KGaA), the content of which is expressly incorporated here by reference.

The size of the depression in comparison to the total tablet is guided by the desired end use of the tablets. Depending on whether a smaller or larger amount of active substance is to be present in the second compressed part, the size of the depression may vary. Irrespective of the end use, in preferred laundry detergent and cleaning product tablets the weight ratio of base tablet to depression filling is within the range from 1:1 to 100:1, preferably from 2:1 to 80:1, with particular preference from 3:1 to 50:1, and in particular from 4:1 to 30:1.

Similar remarks may be made as regards the surface area fractions accounted for by the base tablet and by the depression filling on the total surface area of the tablet. In this case, preference is given to laundry detergent and cleaning product tablets in which the surface area of the impressed depression filling makes up from 1 to 25%, preferably from 2 to 20%, with particular preference from 3 to 15%, and in particular from 4 to 10%, of the total surface area of the filled tablet.

If, for example, the total tablet has dimensions of 20 x 20 x 40 mm and thus a total surface area of 40 cm^2, then preference is given to depression fillings which have a surface area of from 0.4 to 10 cm^2, preferably from 0.8 to 8 cm^2, with particular preference from 1.2 to 6 cm^2, and in particular from 1.6 to 4 cm^2.

The depression filling and the base tablet are preferably colored so as to be visually distinguishable. In addition to visual differentiation, performance advantages may be obtained by virtue of different solubilities of the different regions of the tablet. Laundry detergent and cleaning product tablets in which the impressed depression filling dissolves more rapidly than the base tablet are preferred in accordance with the invention. By incorporating certain constituents, on the one hand, it is possible to accelerate specifically the solubility of the depression filling; secondly, the release of certain ingredients from the depression filling may lead to advantages in the washing or cleaning process. The ingredients which are preferably localized, at least proportionately, in the depression filling are, for example, the below-described disintegration aids, surfactants, enzymes, soil release polymers, builders, bleaches, bleach activators, bleaching catalysts, optical brighteners, silver protectants, etc.

In preferred embodiments of the present invention, the base tablet possesses a high specific weight. Laundry detergent and cleaning product tablets wherein the base tablet has a density of more than 1000 g dm^{-3}, preferably more than 1025 g dm^{-3}, with particular preference more than 1050 g dm^{-3}, and in particular more than 1100 g dm^{-3}, are preferred in accordance with the invention.

Further details relating to physical parameters of the base tablet and of the finished laundry detergent and cleaning product tablets, and information on their production, are given later on below. The preferred ingredients of the base tablet will now be set out.

Laundry detergent and cleaning product tablets which are preferred in the context of the present invention are those wherein the base tablet comprises builders in amounts of from 1 to 100% by weight, preferably from 5 to 95% by weight, with particular preference from 10 to 90% by weight, and in particular from 20 to 85% by weight, based in each case on the weight of the base tablet.

The laundry detergent and cleaning product tablets of the invention may comprise all of the builders commonly used in laundry detergent and cleaning products, i.e., in particular, zeolites, silicates, carbonates, organic cobuilders, and - where there are no ecological prejudices against their use - phosphates as well.

Suitable crystalline, layered sodium silicates possess the general formula $NaMSi_xO_{2x+1}\cdot H_2O$, where M is sodium or hydrogen, x is a number from 1.9 to 4, y is a number from 0 to 20, and preferred values for x are 2, 3 or 4. Crystalline phyllosilicates of this kind are described, for example, in European Patent Application **EP-A-0 164**

514. Preferred crystalline phyllosilicates of the formula indicated are those in which M is sodium and x adopts the value 2 or 3. In particular, both β- and δ-sodium disilicates $Na_2Si_2O_5 \cdot yH_2O$ are preferred, β-sodium disilicate, for example, being obtainable by the process described in International Patent Application **WO-A-91/08171**.

It is also possible to use amorphous sodium silicates having an $Na_2O:SiO_2$ modulus of from 1:2 to 1:3.3, preferably from 1:2 to 1:2.8, and in particular from 1:2 to 1:2.6, which are dissolution-retarded and have secondary washing properties. The retardation of dissolution relative to conventional amorphous sodium silicates may have been brought about in a variety of ways - for example, by surface treatment, compounding, compacting, or overdrying. In the context of this invention, the term "amorphous" also embraces "X-ray-amorphous". This means that in X-ray diffraction experiments the silicates do not yield the sharp X-ray reflections typical of crystalline substances but instead yield at best one or more maxima of the scattered X-radiation, having a width of several degree units of the diffraction angle. However, good builder properties may result, even particularly good builder properties, if the silicate particles in electron diffraction experiments yield vague or even sharp diffraction maxima. The interpretation of this is that the products have microcrystalline regions with a size of from 10 to several hundred nm, values up to max. 50 nm and in particular up to max. 20 nm being preferred. So-called X-ray-amorphous silicates of this kind, which likewise possess retarded dissolution relative to the conventional waterglasses, are described, for example, in German Patent Application **DE-A-44 00 024**. Particular preference is given to compacted amorphous silicates, compounded amorphous silicates, and overdried X-ray-amorphous silicates.

Laundry detergent and cleaning product tablets which are preferred in the context of the present invention are those wherein the base tablet comprises silicate(s), preferably alkali metal silicates, with particular preference crystalline or amorphous alkali metal disilicates, in amounts of from 10 to 60% by weight, preferably from 15 to 50% by weight, and in particular from 20 to 40% by weight, based in each case on the weight of the base tablet.

The finely crystalline, synthetic zeolite used, containing bound water, is preferably zeolite A and/or P. A particularly preferred zeolite P is Zeolite MAP® (commercial product from Crosfield). Also suitable, however, are zeolite X and also mixtures of A, X and/or P. A product available commercially and able to be used with preference in the context of the present invention, for example, is a cocrystallizate of zeolite X and zeolite A (approximately 80% by weight zeolite X), which is sold by CONDEA Augusta S.p.A. under the brand name VEGOBOND AX® and may be described by the formula

$$nNa_2O \cdot (1-n)K_2O \cdot Al_2O_3 \cdot (2-2.5)SiO_2 \cdot (3.5-5.5)H_2O.$$

The zeolite may be used either as a builder in a granular compound or as a kind of "powdering" for the entire mixture intended for compression, it being common to utilize both methods for incorporating the zeolite into the premix. Suitable zeolites have an average particle size of less than 10 µm (volume distribution; measurement method: Coulter counter) and contain preferably from 18 to 22% by weight, in particular from 20 to 22% by weight, of bound water.

Of course, the widely known phosphates may also be used as builder substances provided such a use is not to be

avoided on ecological grounds. Among the large number of commercially available phosphates, the alkali metal phosphates, with particular preference being given to pentasodium and pentapotassium triphosphate (sodium and potassium tripolyphosphate, respectively), possess the greatest importance in the laundry detergent and cleaning product industry.

Alkali metal phosphates is the collective term for the alkali metal (especially sodium and potassium) salts of the various phosphoric acids, among which metaphosphoric acids $(HPO_3)_n$ and orthophosphoric acid H_3PO_4, in addition to higher-molecular-mass representatives, may be distinguished. The phosphates combine a number of advantages: they act as alkali carriers, prevent limescale deposits on machine components, and lime incrustations on fabrics, and additionally contribute to cleaning performance.

Sodium dihydrogen phosphate, NaH_2PO_4, exists as the dihydrate (density 1.91 g cm^{-3}, melting point 60°) and as the monohydrate (density 2.04 g cm^{-3}). Both salts are white powders of very ready solubility in water which lose the water of crystallization on heating and undergo conversion at 200°C into the weakly acidic diphosphate (disodium dihydrogen diphosphate, $Na_2H_2P_2O_7$) and at the higher temperature into sodium trimetaphosphate ($Na_3P_3O_9$) and Maddrell's salt (see below). NaH_2PO_4 reacts acidically; it is formed if phosphoric acid is adjusted to a pH of 4.5 using sodium hydroxide solution and the slurry is sprayed. Potassium dihydrogen phosphate (primary or monobasic potassium phosphate, potassium biphosphate, PDP), KH_2PO_4, is a white salt with a density of 2.33 g cm^{-3}, has a melting point of 253° [decomposition with formation of potassium poly-phosphate $(KPO_3)_x$], and is readily soluble in water.

Disodium hydrogen phosphate (secondary sodium phosphate), Na_2HPO_4, is a colorless, crystalline salt which is very readily soluble in water. It exists in anhydrous form and with 2 mol (density 2.066 g cm^{-3}, water loss at 95°), 7 mol (density 1.68 g cm^{-3}, melting point 48° with loss of 5 H_2O), and 12 mol of water (density 1.52 g cm^{-3}, melting point 35° with loss of 5 H_2O), becomes anhydrous at 100°, and if heated more severely undergoes transition to the diphosphate $Na_4P_2O_7$. Disodium hydrogen phosphate is prepared by neutralizing phosphoric acid with sodium carbonate solution using phenolphthalein as indicator. Dipotassium hydrogen phosphate (secondary or dibasic potassium phosphate), K_2HPO_4, is an amorphous white salt which is readily soluble in water.

Trisodium phosphate, tertiary sodium phosphate, Na_3PO_4, exits as colorless crystals which as the dodecahydrate have a density of 1.62 g cm^{-3} and a melting point of 73-76°C (decomposition), as the decahydrate (corresponding to 19-20% P_2O_5) have a melting point of 100°C, and in anhydrous form (corresponding to 39-40% P_2O_5) have a density of 2.536 g cm^{-3}. Trisodium phosphate is readily soluble in water, with an alkaline reaction, and is prepared by evaporative concentration of a solution of precisely 1 mol of disodium phosphate and 1 mol of NaOH. Tripotassium phosphate (tertiary or tribasic potassium phosphate), K_3PO_4, is a white, deliquescent, granular powder of density 2.56 g cm^{-3}, has a melting point of 1340°, and is readily soluble in water with an alkaline reaction. It is produced, for example, when Thomas slag is heated with charcoal and potassium sulfate. Despite the relatively high price, the more readily soluble and therefore highly active potassium phosphates are frequently preferred in the cleaning products industry over the corresponding sodium compounds.

Tetrasodium diphosphate (sodium pyrophosphate), $Na_4P_2O_7$, exists in anhydrous form (density 2.534 g cm^{-3}, melting point 988°, 880° also reported) and as the decahydrate (density 1.815-1.836 g cm^{-3}, melting point 94° with loss of water). Both substances are colorless crystals which dissolve in water with an alkaline reaction. $Na_4P_2O_7$ is formed when disodium phosphate is heated at > 200° or by reacting phosphoric acid with sodium carbonate in stoichiometric ratio and dewatering the solution by spraying. The decahydrate complexes heavy metal salts and water hardeners and therefore reduces the hardness of the water. Potassium diphosphate (potassium pyrophosphate), $K_4P_2O_7$, exists in the form of the trihydrate and is a colorless, hygroscopic powder of density 2.33 g cm^{-3} which is soluble in water, the pH of the 1% strength solution at 25° being 10.4.

Condensation of NaH_2PO_4 or of KH_2PO_4 gives rise to higher-molecular-mass sodium and potassium phosphates, among which it is possible to distinguish cyclic representatives, the sodium and potassium metaphosphates, and catenated types, the sodium and potassium polyphosphates. For the latter in particular a large number of names are in use: fused or calcined phosphates, Graham's salt, Kurrol's and Maddrell's salt. All higher sodium and potassium phosphates are referred to collectively as condensed phosphates.

The industrially important pentasodium triphosphate, $Na_5P_3O_{10}$ (sodium tripolyphosphate), is a nonhygroscopic, white, water-soluble salt which is anhydrous or crystallizes with 6 H_2O and has the general formula $NaO-[P(O)(ONa)-O]_n-Na$ where n = 3. About 17 g of the anhydrous salt dissolve in 100 g of water at room temperature, at 60° about 20 g, at 100° around 32 g; after heating the solution at 100°C for two hours, about 8% orthophosphate and 15% diphosphate are produced by hydrolysis. For the preparation of

pentasodium triphosphate, phosphoric acid is reacted with sodium carbonate solution or sodium hydroxide solution in stoichiometric ratio and the solution is dewatered by spraying. In a similar way to Graham's salt and sodium diphosphate, pentasodium triphosphate dissolves numerous insoluble metal compounds (including lime soaps, etc). Pentapotassium triphosphate, $K_5P_3O_{10}$ (potassium tripolyphosphate), is commercialized, for example, in the form of a 50% strength by weight solution (> 23% P_2O_5, 25% K_2O). The potassium polyphosphates find broad application in the laundry detergents and cleaning products industry. There also exist sodium potassium tripolyphosphates, which may likewise be used for the purposes of the present invention. These are formed, for example, when sodium trimetaphosphate is hydrolyzed with KOH:

$$(NaPO_3)_3 + 2\ KOH \rightarrow Na_3K_2P_3O_{10} + H_2O$$

They can be used in accordance with the invention in precisely the same way as sodium tripolyphospate, potassium tripolyphosphate, or mixtures of these two; mixtures of sodium tripolyphosphate and sodium potassium tripolyphosphate, or mixtures of potassium tripolyphosphate and sodium potassium tripolyphosphate, or mixtures of sodium tripolyphosphate and potassium tripolyphosphate and sodium potassium tripolyphospate, may also be used in accordance with the invention.

Laundry detergent and cleaning product tablets which are preferred in the context of the present invention are those wherein the base tablet comprises phosphate(s), preferably alkali metal phosphate(s), with particular preference pentasodium or pentapotassium triphosphate (sodium or potassium tripolyphosphate), in amounts of from 20 to 80% by weight, preferably from 25 to 75% by weight, and in

particular from 30 to 70% by weight, based in each case on the weight of the base tablet.

Further constituents present may be alkali metal carriers. Alkali metal carriers are, for example, alkali metal hydroxides, alkali metal carbonates, alkali metal hydrogen carbonates, alkali metal sesquicarbonates, the abovementioned alkali silicates, alkali metal metasilicates and mixtures of the abovementioned substances, preference being given in the context of this invention to the use of the alkali metal carbonates, especially sodium carbonate, sodium hydrogen carbonate, or sodium sesquicarbonate. Particular preference is given to a builder system comprising a mixture of tripolyphosphate and sodium carbonate. Likewise particularly preferred is a builder system comprising a mixture of tripolyphosphate and sodium carbonate and sodium disilicate.

In particularly preferred laundry detergent and cleaning product tablets, the base tablet comprises carbonate(s) and/or hydrogen carbonate(s), preferably alkali metal carbonates, with particular preference sodium carbonate, in amounts of from 5 to 50% by weight, preferably from 7.5 to 40% by weight, and in particular from 10 to 30% by weight, based in each case on the weight of the base tablet.

Organic cobuilders which may be used in the laundry detergent and cleaning product tablets of the invention are, in particular, polycarboxylates/polycarboxylic acids, polymeric polycarboxylates, aspartic acid, polyacetals, dextrins, further organic cobuilders (see below), and phosphonates. These classes of substance are described below.

Organic builder substances which may be used are, for example, the polycarboxylic acids, usable in the form

of their sodium salts, the term polycarboxylic acids meaning those carboxylic acids which carry more than one acid function. Examples of these are citric acid, adipic acid, succinic acid, glutaric acid, malic acid, tartaric acid, maleic acid, fumaric acid, sugar acids, amino carboxylic acids, nitrilotriacetic acid (NTA), provided such use is not objectionable on ecological grounds, and also mixtures thereof. Preferred salts are the salts of the polycarboxylic acids such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids, and mixtures thereof.

The acids per se may also be used. In addition to their builder effect, the acids typically also possess the property of an acidifying component and thus also serve to establish a lower and milder pH of laundry detergents or cleaning products. In this context, mention may be made in particular of citric acid, succinic acid, glutaric acid, adipic acid, gluconic acid, and any desired mixtures thereof.

Also suitable as builders are polymeric polycarboxylates; these are, for example, the alkali metal salts of polyacrylic acid or of polymethacrylic acid, examples being those having a relative molecular mass of from 500 to 70,000 g/mol.

The molecular masses reported for polymeric polycarboxylates, for the purposes of this document, are weight-average molecular masses, M_w, of the respective acid form, determined basically by means of gel permeation chromatography (GPC) using a UV detector. The measurement was made against an external polyacrylic acid standard, which owing to its structural similarity to the polymers under investigation provides realistic molecular weight values. These figures differ markedly from the molecular weight values obtained using poly-

styrenesulfonic acids as the standard. The molecular masses measured against polystyrenesulfonic acids are generally much higher than the molecular masses reported in this document.

Suitable polymers are, in particular, polyacrylates, which preferably have a molecular mass of from 2000 to 20,000 g/mol. Owing to their superior solubility, preference in this group may be given in turn to the short-chain polyacrylates, which have molecular masses of from 2000 to 10,000 g/mol, and with particular preference from 3000 to 5000 g/mol.

Also suitable are copolymeric polycarboxylates, especially those of acrylic acid with methacrylic acid and of acrylic acid or methacrylic acid with maleic acid. Copolymers which have been found particularly suitable are those of acrylic acid with maleic acid which contain from 50 to 90% by weight acrylic acid and from 50 to 10% by weight maleic acid. Their relative molecular mass, based on free acids, is generally from 2000 to 70,000 g/mol, preferably from 20,000 to 50,000 g/mol, and in particular from 30,000 to 40,000 g/mol.

The (co)polymeric polycarboxylates can be used either as powders or as aqueous solutions. The (co)polymeric polycarboxylate content of the compositions is preferably from 0.5 to 20% by weight, in particular from 3 to 10% by weight.

In order to improve the solubility in water, the polymers may also contain allylsulfonic acids, such as allyloxybenzenesulfonic acid and methallylsulfonic acid, for example, as monomers.

Particular preference is also given to biodegradable polymers comprising more than two different monomer

units, examples being those comprising, as monomers, salts of acrylic acid and of maleic acid, and also vinyl alcohol or vinyl alcohol derivatives, or those comprising, as monomers, salts of acrylic acid and of 2-alkylallylsulfonic acid, and also sugar derivatives.

Further preferred copolymers are those described in German Patent Applications **DE-A-43 03 320** and **DE-A-44 17 734**, whose monomers are preferably acrolein and acrylic acid/acrylic acid salts, and, respectively, acrolein and vinyl acetate.

Similarly, further preferred builder substances that may be mentioned include polymeric amino dicarboxylic acids, their salts or their precursor substances. Particular preference is given to polyaspartic acids and their salts and derivatives, which are disclosed in German Patent Application **DE-A-195 40 086** to have not only cobuilder properties but also a bleach-stabilizing action.

Further suitable builder substances are polyacetals, which may be obtained by reacting dialdehydes with polyol carboxylic acids having 5 to 7 carbon atoms and at least 3 hydroxyl groups. Preferred polyacetals are obtained from dialdehydes such as glyoxal, glutaraldehyde, terephthalaldehyde and mixtures thereof and from polyol carboxylic acids such as gluconic acid and/or glucoheptonic acid.

Further suitable organic builder substances are dextrins, examples being oligomers and polymers of carbohydrates, which may be obtained by partial hydrolysis of starches. The hydrolysis can be conducted by customary processes; for example, acid-catalyzed or enzyme-catalyzed processes. The hydrolysis products preferably have average molecular masses in the range from 400 to 500,000 g/mol. Preference is given here to

a polysaccharide having a dextrose equivalent (DE) in the range from 0.5 to 40, in particular from 2 to 30, DE being a common measure of the reducing effect of a polysaccharide in comparison to dextrose, which possesses a DE of 100. It is possible to use both maltodextrins having a DE of between 3 and 20 and dried glucose syrups having a DE of between 20 and 37, and also so-called yellow dextrins and white dextrins having higher molecular masses, in the range from 2000 to 30,000 g/mol.

The oxidized derivatives of such dextrins comprise their products of reaction with oxidizing agents which are able to oxidize at least one alcohol function of the saccharide ring to the carboxylic acid function. Oxidized dextrins of this kind, and processes for preparing them, are known, for example, from European Patent Applications **EP-A-0 232 202, EP-A-0 427 349, EP-A-0 472 042** and **EP-A-0 542 496** and from International Patent Applications **WO 92/18542, WO 93/08251, WO 93/16110, WO 94/28030, WO 95/07303, WO 95/12619** and **WO 95/20608**. Likewise suitable is an oxidized oligosaccharide in accordance with German Patent Application **DE-A-196 00 018**. A product oxidized at C_6 of the saccharide ring may be particularly advantageous.

Oxydisuccinates and other derivatives of disuccinates, preferably ethylenediamine disuccinate, are further suitable cobuilders. Ethylenediamine N,N'-disuccinate (EDDS) is used preferably in the form of its sodium or magnesium salts. Further preference in this context is given to glycerol disuccinates and glycerol trisuccinates as well. Suitable use amounts in formulations containing zeolite and/or silicate are from 3 to 15% by weight.

Examples of further useful organic cobuilders are acetylated hydroxy carboxylic acids and their salts, which may also be present in lactone form and which contain at least 4 carbon atoms, at least one hydroxyl group, and not more than two acid groups. Such cobuilders are described, for example, in International Patent Application **WO 95/20029**.

A further class of substance having cobuilder properties is represented by the phosphonates. The phosphonates in question are, in particular, hydroxyalkane- and aminoalkanephosphonates. Among the hydroxyalkanephosphonates, 1-hydroxyethane-1,1-diphosphonate (HEDP) is of particular importance as a cobuilder. It is used preferably as the sodium salt, the disodium salt being neutral and the tetrasodium salt giving an alkaline (pH 9) reaction. Suitable aminoalkanephosphonates are preferably ethylenediaminetetramethylenephosphonate (EDTMP), diethylenetriaminepentamethylenephosphonate (DTPMP), and their higher homologs. They are used preferably in the form of the neutrally reacting sodium salts, e.g., as the hexasodium salt of EDTMP or as the hepta- and octasodium salt of DTPMP. As a builder in this case, preference is given to using HEDP from the class of the phosphonates. Furthermore, the aminoalkanephosphonates possess a pronounced heavy metal binding capacity. Accordingly, and especially if the compositions also contain bleach, it may be preferred to use aminoalkanephosphonates, expecially DTPMP, or to use mixtures of said phosphonates.

Furthermore, all compounds capable of forming complexes with alkaline earth metal ions may be used as cobuilders.

The amount of builder is usually between 10 and 70% by weight, preferably between 15 and 60% by weight, and in

particular between 20 and 50% by weight. In turn, the amount of builders used is dependent on the intended use, so that bleach tablets may contain higher amounts of builders (for example, between 20 and 70% by weight, preferably between 25 and 65% by weight, and in particular between 30 and 55% by weight) than, say, laundry detergent tablets (usually from 10 to 50% by weight, preferably from 12.5 to 45% by weight, and in particular between 17.5 and 37.5% by weight).

Preferred laundry detergent and cleaning product tablets further comprise one or more surfactants. In the laundry detergent and cleaning product tablets of the invention it is possible to use anionic, nonionic, cationic and/or amphoteric surfactants, and/or mixtures thereof. From a performance standpoint, preference is given for laundry detergent tablets to mixtures of anionic and nonionic surfactants. The total surfactant content of the tablets is from 5 to 60% by weight, based on the tablet weight, preference being given to surfactant contents of more than 15% by weight, while cleaning product tablets for machine dishwashing contain preferably less than 5% by weight of surfactant(s).

Anionic surfactants used are, for example, those of the sulfonate and sulfate type. Preferred surfactants of the sulfonate type are C_{9-13} alkylbenzenesulfonates, olefinsulfonates, i.e., mixtures of alkenesulfonates and hydroxyalkanesulfonates, and also disulfonates, as are obtained, for example, from C_{12-18} monoolefins having a terminal or internal double bond by sulfonating with gaseous sulfur trioxide followed by alkaline or acidic hydrolysis of the sulfonation products. Also suitable are alkanesulfonates, which are obtained from C_{12-18} alkanes, for example, by sulfochlorination or sulfoxidation with subsequent hydrolysis or neutralization, respectively. Likewise suitable, in

addition, are the esters of α-sulfo fatty acids (ester sulfonates), e.g., the α-sulfonated methyl esters of hydrogenated coconut, palm kernel or tallow fatty acids.

Further suitable anionic surfactants are sulfated fatty acid glycerol esters. Fatty acid glycerol esters are the monoesters, diesters and triesters, and mixtures thereof, as obtained in the preparation by esterification of a monoglycerol with from 1 to 3 mol of fatty acid or in the transesterification of triglycerides with from 0.3 to 2 mol of glycerol. Preferred sulfated fatty acid glycerol esters are the sulfation products of saturated fatty acids having 6 to 22 carbon atoms, examples being those of caproic acid, caprylic acid, capric acid, myristic acid, lauric acid, palmitic acid, stearic acid, or behenic acid.

Preferred alk(en)yl sulfates are the alkali metal salts, and especially the sodium salts, of the sulfuric monoesters of C_{12}-C_{18} fatty alcohols, examples being those of coconut fatty alcohol, tallow fatty alcohol, lauryl, myristyl, cetyl or stearyl alcohol, or of C_{10}-C_{20} oxo alcohols, and those monoesters of secondary alcohols of these chain lengths. Preference is also given to alk(en)yl sulfates of said chain length which contain a synthetic straight-chain alkyl radical prepared on a petrochemical basis, these sulfates possessing degradation properties similar to those of the corresponding compounds based on fatty-chemical raw materials. From a detergents standpoint, the C_{12}-C_{16} alkyl sulfates and C_{12}-C_{15} alkyl sulfates, and also C_{14}-C_{15} alkyl sulfates, are preferred. In addition, 2,3-alkyl sulfates, which may for example be prepared in accordance with US Patents 3,234,258 or 5,075,041 and obtained as commercial products from Shell Oil Company under the name DAN®, are suitable anionic surfactants.

Also suitable are the sulfuric monoesters of the straight-chain or branched C_{7-21} alcohols ethoxylated with from 1 to 6 mol of ethylene oxide, such as 2-methyl-branched C_{9-11} alcohols containing on average 3.5 mol of ethylene oxide (EO) or C_{12-18} fatty alcohols containing from 1 to 4 EO. Because of their high foaming behavior they are used in cleaning products only in relatively small amounts, for example, in amounts of from 1 to 5% by weight.

Further suitable anionic surfactants include the salts of alkylsulfosuccinic acid, which are also referred to as sulfosuccinates or as sulfosuccinic esters and which constitute monoesters and/or diesters of sulfosuccinic acid with alcohols, preferably fatty alcohols and especially ethoxylated fatty alcohols. Preferred sulfosuccinates comprise C_{8-18} fatty alcohol radicals or mixtures thereof. Especially preferred sulfosuccinates contain a fatty alcohol radical derived from ethoxylated fatty alcohols which themselves represent nonionic surfactants (for description, see below). Particular preference is given in turn to sulfosuccinates whose fatty alcohol radicals are derived from ethoxylated fatty alcohols having a narrowed homolog distribution. Similarly, it is also possible to use alk(en)ylsuccinic acid containing preferably 8 to 18 carbon atoms in the alk(en)yl chain, or salts thereof.

Further suitable anionic surfactants are, in particular, soaps. Suitable soaps include saturated fatty acid soaps, such as the salts of lauric acid, myristic acid, palmitic acid, stearic acid, hydrogenated erucic acid and behenic acid, and, in particular, mixtures of soaps derived from natural fatty acids, e.g., coconut, palm kernel, or tallow fatty acids.

The anionic surfactants, including the soaps, may be present in the form of their sodium, potassium or ammonium salts and also as soluble salts of organic bases, such as mono-, di- or triethanolamine. Preferably, the anionic surfactants are in the form of their sodium or potassium salts, in particular in the form of the sodium salts.

Nonionic surfactants used are preferably alkoxylated, advantageously ethoxylated, especially primary, alcohols having preferably 8 to 18 carbon atoms and on average from 1 to 12 mol of ethylene oxide (EO) per mole of alcohol, in which the alcohol radical may be linear or, preferably, methyl-branched in position 2 and/or may comprise linear and methyl-branched radicals in a mixture, as are commonly present in oxo alcohol radicals. In particular, however, preference is given to alcohol ethoxylates containing linear radicals from alcohols of natural origin having 12 to 18 carbon atoms, e.g., from coconut, palm, tallow fatty or oleyl alcohol and on average from 2 to 8 EO per mole of alcohol. Preferred ethoxylated alcohols include, for example, C_{12-14} alcohols containing 3 EO or 4 EO, C_{9-11} alcohol containing 7 EO, C_{13-15} alcohols containing 3 EO, 5 EO, 7 EO or 8 EO, C_{12-18} alcohols containing 3 EO, 5 EO or 7 EO, and mixtures thereof, such as mixtures of C_{12-14} alcohol containing 3 EO and C_{12-18} alcohol containing 5 EO. The stated degrees of ethoxylation represent statistical mean values, which for a specific product may be an integer or a fraction. Preferred alcohol ethoxylates have a narrowed homolog distribution (narrow range ethoxylates, NREs). In addition to these nonionic surfactants it is also possible to use fatty alcohols containing more than 12 EO. Examples thereof are tallow fatty alcohol containing 14 EO, 25 EO, 30 EO or 40 EO.

As further nonionic surfactants, furthermore, use may also be made of alkyl glycosides of the general formula $RO(G)_x$, where R is a primary straight-chain or methyl-branched aliphatic radical, especially an aliphatic radical methyl-branched in position 2, containing 8 to 22, preferably 12 to 18, carbon atoms, and G is the symbol representing a glycose unit having 5 or 6 carbon atoms, preferably glucose. The degree of oligomerization, x, which indicates the distribution of monoglycosides and oligoglycosides, is any desired number between 1 and 10; preferably, x is from 1.2 to 1.4.

A further class of nonionic surfactants used with preference, which are used either as sole nonionic surfactant or in combination with other nonionic surfactants, are alkoxylated, preferably ethoxylated, or ethoxylated and propoxylated, fatty acid alkyl esters, preferably having 1 to 4 carbon atoms in the alkyl chain, especially fatty acid methyl esters, as are described, for example, in Japanese Patent Application JP 58/217598, or those prepared preferably by the process described in International Patent Application WO-A-90/13533.

Nonionic surfactants of the amine oxide type, examples being N-cocoalkyl-N,N-dimethylamine oxide and N-tallowalkyl-N,N-dihydroxyethylamine oxide, and of the fatty acid alkanolamide type, may be also be suitable. The amount of these nonionic surfactants is preferably not more than that of the ethoxylated fatty alcohols, in particular not more than half thereof.

Further suitable surfactants are polyhydroxy fatty acid amides of the formula (I),

$$\begin{array}{l} R^1 \\ | \\ R\text{-}CO\text{-}N\text{-}[Z] \end{array} \qquad (I)$$

where RCO is an aliphatic acyl radical having 6 to 22 carbon atoms, R^1 is hydrogen or an alkyl or hydroxyalkyl radical having 1 to 4 carbon atoms, and [Z] is a linear or branched polyhydroxyalkyl radical having 3 to 10 carbon atoms and from 3 to 10 hydroxyl groups. The polyhydroxy fatty acid amides are known substances which are customarily obtainable by reductive amination of a reducing sugar with ammonia, an alkylamine or an alkanolamine, and subsequent acylation with a fatty acid, a fatty acid alkyl ester or a fatty acid chloride.

The group of the polyhydroxy fatty acid amides also includes compounds of the formula (II)

$$\begin{array}{l} R^1\text{-}O\text{-}R^2 \\ | \\ R\text{-}CO\text{-}N\text{-}[Z] \end{array} \qquad (II)$$

where R is a linear or branched alkyl or alkenyl radical having 7 to 12 carbon atoms, R^1 is a linear, branched or cyclic alkyl radical or an aryl radical having 2 to 8 carbon atoms and R^2 is a linear, branched or cyclic alkyl radical or an aryl radical or an oxyalkyl radical having 1 to 8 carbon atoms, preference being given to C_{1-4} alkyl radicals or phenyl radicals, and [Z] is a linear polyhydroxyalkyl radical whose alkyl chain is substituted by at least two hydroxyl groups, or alkoxylated, preferably ethoxylated or propoxylated, derivatives of said radical.

[Z] is preferably obtained by reductive amination of a reduced sugar, e.g., glucose, fructose, maltose, lactose, galactose, mannose, or xylose. The N-alkoxy-

or N-aryloxy-substituted compounds may then be converted to the desired polyhydroxy fatty acid amides, for example, in accordance with the teaching of International Patent Application WO-A-95/07331 by reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst.

In the context of the present invention, preference is given to laundry detergent and cleaning product tablets comprising anionic and nonionic surfactant(s); performance advantages may result from certain proportions in which the individual classes of surfactant are used.

For example, particular preference is given to laundry detergent and cleaning product tablets in which the ratio of anionic surfactant(s) to nonionic surfactant(s) is between 10:1 and 1:10, preferably between 7.5:1 and 1:5, and in particular between 5:1 and 1:2. Also preferred are laundry detergent and cleaning product tablets comprising, as surfactant(s), preferably anionic and/or nonionic surfactant(s) in amounts of from 5 to 40% by weight, preferably from 7.5 to 35% by weight, with particular preference from 10 to 30% by weight, and in particular from 12.5 to 25% by weight, based in each case on the tablet weight.

From a performance standpoint it may be advantageous if certain classes of surfactant are absent from some phases of the laundry detergent and cleaning product tablets or from the tablet as a whole, i.e., from all phases. A further important embodiment of the present invention therefore envisages that at least one phase of the tablets is free from nonionic surfactants.

Conversely, however, the presence of certain surfactants in individual phases or in the whole tablet, i.e., in all phases, may produce a positive

effect. The incorporation of the above-described alkyl polyglycosides has been found advantageous, and so preference is given to laundry detergent and cleaning product tablets in which at least one phase of the tablets comprises alkyl polyglycosides.

Similarly to the case with the nonionic surfactants, the omission of anionic surfactants from certain phases or all phases may also result in laundry detergent and cleaning product tablets better suited to certain fields of application. In the context of the present invention, therefore, it is also possible to conceive of laundry detergent and cleaning product tablets in which at least one phase of the tablet is free from anionic surfactants.

As already mentioned, the use of surfactants in the case of cleaning product tablets for machine dishwashing is preferably limited to the use of nonionic surfactants in small amounts. Laundry detergent and cleaning product tablets preferred for use as cleaning product tablets in the context of the present invention are those wherein the base tablet has total surfactant contents of less than 5% by weight, preferably less than 4% by weight, with particular preference less than 3% by weight, and in particular less than 2% by weight, based in each case on the weight of the base tablet. Surfactants used in machine dishwashing compositions are usually only low-foaming nonionic surfactants. Representatives from the groups of the anionic, cationic and amphoteric surfactants, in contrast, are of relatively little importance. With particular preference, the cleaning product tablets of the invention for machine dishwashing comprise nonionic surfactants, especially nonionic surfactants from the group of the alkoxylated alcohols. Preferred nonionic surfactants used are alkoxylated, advantageously ethoxylated, especially primary alcohols having

preferably 8 to 18 carbon atoms and on average from 1 to 12 mol of ethylene oxide (EO) per mole of alcohol, in which the alcohol radical may be linear or, preferably, methyl-branched in position 2 and/or may contain a mixture of linear and methyl-branched radicals, as are customarily present in oxo alcohol radicals. Particular preference is given, however, to alcohol ethoxylates having linear radicals from alcohols of natural origin having 12 to 18 carbon atoms, e.g., from coconut, palm, tallow fatty or oleyl alcohol, and having on average from 2 to 8 EO per mole of alcohol. The preferred ethoxylated alcohols include, for example, C_{12-14} alcohols having 3 EO or 4 EO, C_{9-11} alcohol having 7 EO, C_{13-15} alcohols having 3 EO, 5 EO, 7 EO or 8 EO, C_{12-18} alcohols having 3 EO, 5 EO or 7 EO, and mixtures of these, such as mixtures of C_{12-14} alcohol having 3 EO and C_{12-18} alcohol having 5 EO. The stated degrees of ethoxylation are statistical means, which for a specific product may be an integer or a fraction. Preferred alcohol ethoxylates have a narrowed homolog distribution (narrow range ethoxylates, NREs). In addition to these nonionic surfactants, fatty alcohols having more than 12 EO may also be used. Examples thereof are tallow fatty alcohol having 14 EO, 25 EO, 30 EO, or 40 EO.

In order to facilitate the disintegration of highly compacted tablets, it is possible to incorporate disintegration aids, known as tablet disintegrants, into the tablets in order to reduce the disintegration times. Tablet disintegrants, or disintegration accelerators, are understood in accordance with Römpp (9th Edition, Vol. 6, p. 440) and Voigt "*Lehrbuch der pharmazeutischen Technologie*" [Textbook of pharmaceutical technology] (6th Edition, 1987, pp. 182-184) to be auxiliaries which ensure the rapid disintegration of tablets in water or gastric fluid and the release of the drugs in absorbable form.

These substances increase in volume on ingress of water, with on the one hand an increase in the intrinsic volume (swelling) and on the other hand, by way of the release of gases, the generation of a pressure which causes the tablets to disintegrate into smaller particles. Examples of established disintegration aids are carbonate/citric acid systems, with the use of other organic acids also being possible. Examples of swelling disintegration aids are synthetic polymers such as polyvinylpyrrolidone (PVP) or natural polymers and/or modified natural substances such as cellulose and starch and their derivatives, alginates, or casein derivatives.

Preferred laundry detergent and cleaning product tablets contain from 0.5 to 10% by weight, preferably from 3 to 7% by weight, and in particular from 4 to 6% by weight, of one or more disintegration aids, based in each case on the tablet weight. If only the base tablet comprises disintegration aids, then these figures are based only on the weight of the base tablet.

Preferred disintegrants used in the context of the present invention are cellulose-based disintegrants and so preferred laundry detergent and cleaning product tablets comprise a cellulose-based disintegrant of this kind in amounts from 0.5 to 10% by weight, preferably from 3 to 7% by weight, and in particular from 4 to 6% by weight. Pure cellulose has the formal empirical composition $(C_6H_{10}O_5)_n$ and, considered formally, is a β-1,4-polyacetal of cellobiose, which itself is constructed of two molecules of glucose. Suitable celluloses consist of from about 500 to 5000 glucose units and, accordingly, have average molecular masses of from 50,000 to 500,000. Cellulose-based disintegrants which can be used also include, in the context of the present invention, cellulose derivatives

obtainable by polymer-analogous reactions from cellulose. Such chemically modified celluloses include, for example, products of esterifications and etherifications in which hydroxy hydrogen atoms have been substituted. However, celluloses in which the hydroxy groups have been replaced by functional groups not attached by an oxygen atom may also be used as cellulose derivatives. The group of the cellulose derivatives embraces, for example, alkali metal celluloses, carboxymethylcellulose (CMC), cellulose esters and cellulose ethers and aminocelluloses. Said cellulose derivatives are preferably not used alone as cellulose-based disintegrants but instead are used in a mixture with cellulose. The cellulose derivative content of these mixtures is preferably less than 50% by weight, with particular preference less than 20% by weight, based on the cellulose-based disintegrant. The particularly preferred cellulose-based disintegrant used is pure cellulose, free from cellulose derivatives.

The cellulose used as disintegration aid is preferably not used in finely divided form but instead is converted into a coarser form, for example, by granulation or compaction, before being admixed to the premixes intended for compression. Laundry detergent and cleaning product tablets comprising disintegrants in granular or optionally cogranulated form are described in German Patent Applications **DE 197 09 991** (Stefan Herzog) and **DE 197 10 254** (Henkel) and in International Patent Application **WO98/40463** (Henkel). These documents also provide further details on the production of granulated, compacted or cogranulated cellulose disintegrants. The particle sizes of such disintegrants are usually above 200 µm, preferably between 300 and 1600 µm to the extent of at least 90%, and in particular between 400 and 1200 µm to the extent of at least 90%. The

abovementioned, relatively coarse disintegration aids, and those described in more detail in the cited documents, are preferred for use as disintegration aids in the context of the present invention and are available commercially, for example, under the designation Arbocel® TF-30-HG from the company Rettenmaier.

As a further cellulose-based disintegrant or as a constituent of this component it is possible to use microcrystalline cellulose. This microcrystalline cellulose is obtained by partial hydrolysis of celluloses under conditions which attack only the amorphous regions (approximately 30% of the total cellulose mass) of the celluloses and break them up completely but leave the crystalline regions (approximately 70%) intact. Subsequent deaggregation of the microfine celluloses resulting from the hydrolysis yields the microcrystalline celluloses, which have primary particle sizes of approximately 5 µm and can be compacted, for example, to granules having an average particle size of 200 µm.

Laundry detergent and cleaning product tablets which are preferred in the context of the present invention further comprise a disintegration aid, preferably a cellulose-based disintegration aid, preferably in granular, cogranulated or compacted form, in amounts of from 0.5 to 10% by weight, preferably from 3 to 7% by weight, and in particular from 4 to 6% by weight, based in each case on the tablet weight.

The laundry detergent and cleaning product tablets of the invention may further comprise, both in the base tablet and in the depression filling, a gas-evolving effervescent system. Said gas-evolving effervescent system may consist of a single substance which on contact with water releases a gas. Among these

compounds mention may be made, in particular, of magnesium peroxide, which on contact with water releases oxygen. Normally, however, the gas-releasing effervescent system consists in its turn of at least two constituents which react with one another and, in so doing, form gas. Although a multitude of systems which release, for example, nitrogen, oxygen or hydrogen are conceivable and offerable here, the effervescent system used in the laundry detergent and cleaning product tablets of the invention will be selectable on the basis of both economic and environmental considerations. Preferred effervescent systems consist of alkali metal carbonate and/or alkali metal hydrogen carbonate and of an acidifier apt to release carbon dioxide from the alkali metal salts in aqueous solution.

Among the alkali metal carbonates and/or alkali metal hydrogen carbonates, the sodium and potassium salts are much preferred over the other salts on grounds of cost. It is of course not mandatory to use the single alkali metal carbonates or alkali metal hydrogen carbonates in question; rather, mixtures of different carbonates and hydrogen carbonates may be preferred from the standpoint of wash technology.

In preferred laundry detergent and cleaning product tablets, the effervescent system used comprises from 2 to 20% by weight, preferably from 3 to 15% by weight, and in particular from 5 to 10% by weight, of an alkali metal carbonate or alkali metal hydrogen carbonate, and from 1 to 15, preferably from 2 to 12, and in particular from 3 to 10, % by weight of an acidifier, based in each case on the total tablet.

As examples of acidifiers which release carbon dioxide from the alkali metal salts in aqueous solution it is possible to use boric acid and also alkali metal

hydrogen sulfates, alkali metal hydrogen phosphates, and other inorganic salts. Preference is given, however, to the use of organic acidifiers, with citric acid being a particularly preferred acidifier. However, it is also possible, in particular, to use the other solid mono-, oligo- and polycarboxylic acids. Preferred among this group, in turn, are tartaric acid, succinic acid, malonic acid, adipic acid, maleic acid, fumaric acid, oxalic acid, and polyacrylic acid. Organic sulfonic acids such as amidosulfonic acid may likewise be used. A commercially available acidifier which is likewise preferred for use in the context of the present invention is Sokalan® DCS (trademark of BASF), a mixture of succinic acid (max. 31% by weight), glutaric acid (max. 50% by weight), and adipic acid (max. 33% by weight).

In the context of the present invention, preference is given to laundry detergent and cleaning product tablets where the acidifier used in the effervescent system comprises a substance from the group of the organic di-, tri- and oligocarboxylic acids, or mixtures thereof.

In addition to the abovementioned constituents, builder, surfactant and disintegration aid, the laundry detergent and cleaning product tablets of the invention may further comprise further customary laundry detergent and cleaning product ingredients from the group consisting of bleaches, bleach activators, dyes, fragrances, optical brighteners, enzymes, foam inhibitors, silicone oils, antiredeposition agents, graying inhibitors, color transfer inhibitors, and corrosion inhibitors.

Among the compounds used as bleaches which yield H_2O_2 in water, particular importance is possessed by sodium perborate tetrahydrate and sodium perborate

monohydrate. Further bleaches which may be used are, for example, sodium percarbonate, peroxypyrophosphates, citrate perhydrates, and H_2O_2-donating peracidic salts or peracids, such as perbenzoates, peroxophthalates, diperazelaic acid, phthaloiminoper acid or diperdodecanedioic acid. Cleaning products of the invention may also comprise bleaches from the group of organic bleaches. Typical organic bleaches are the diacyl peroxides, such as dibenzoyl peroxide, for example. Further typical organic bleaches are the peroxy acids, particular examples being the alkyl peroxy acids and the aryl peroxy acids. Preferred representatives are (a) peroxybenzoic acid and its ring-substituted derivatives, such as alkylperoxybenzoic acids, and also peroxy-α-naphthoic acid and magnesium monoperphthalate, (b) aliphatic or substituted aliphatic peroxy acids, such as peroxylauric acid, peroxystearic acid, ε-phthalimidoperoxy caproic acid [phthaloiminoperoxyhexanoic acid (PAP)], o-carboxybenzamidoperoxycaproic acid, N-nonenylamidoperadipic acid and N-nonenylamidopersuccinates, and (c) aliphatic and araliphatic peroxy dicarboxylic acids, such as 1,12-diperoxydecanedicarboxylic acid, 1,9-diperoxyazelaic acid, diperoxysebacic acid, diperoxybrassylic acid, the diperoxyphthalic acids, 2-decyldiperoxybutane-1,4-dioic acid and N,N-terephthaloyldi(6-aminopercaproic acid) may be used.

Bleaches in the cleaning product tablets of the invention for machine dishwashing may also be substances which release chlorine or bromine. Among suitable chlorine- or bromine-releasing materials, examples include heterocyclic N-bromoamides and N-chloroamides, examples being trichloroisocyanuric acid, tribromoisocyanuric acid, dibromoisocyanuric acid and/or dichloroisocyanuric acid (DICA) and/or salts thereof with cations such as potassium and sodium.

Hydantoin compounds, such as 1,3-dichloro-5,5-dimethylhydantoin, are likewise suitable.

The bleaches are used in machine dishwashing compositions usually in amounts of from 1 to 30% by weight, preferably from 2.5 to 20% by weight, and in particular from 5 to 15% by weight, based in each case on the composition. In the context of the present invention, these proportions relate to the weight of the base tablet.

Bleach activators, which boost the action of the bleaches, may likewise be a constituent of the base tablet. Known bleach activators are compounds containing one or more N-acyl and/or O-acyl groups, such as substances from the class of the anhydrides, esters, imides and acylated imidazoles or oximes. Examples are tetraacetylethylenediamine TAED, tetra-acetylmethylene-diamine TAMD, and tetraacetyl-hexylenediamine TAHD, and also pentaacetylglucose PAG, 1,5-diacetyl-2,2-dioxohexahydro-1,3,5-triazine DADHT, and isatoic anhydride ISA.

Bleach activators which may be used are compounds which under perhydrolysis conditions give rise to aliphatic peroxo carboxylic acids having preferably 1 to 10 carbon atoms, in particular 2 to 4 carbon atoms, and/or substituted or unsubstituted perbenzoic acid. Suitable substances are those which carry O-acyl and/or N-acyl groups of the stated number of carbon atoms, and/or substituted or unsubstituted benzoyl groups. Preference is given to polyacylated alkylenediamines, especially tetraacetylethylenediamine (TAED), acylated triazine derivatives, especially 1,5-diacetyl-2,4-dioxohexa-hydro-1,3,5-triazine (DADHT), acylated glycolurils, especially tetraacetylglycoluril (TAGU), N-acyl imides, especially N-nonanoylsuccinimide (NOSI), acylated phenolsulfonates, especially n-nonanoyl- or

isononanoyloxybenzenesulfonate (n- or iso-NOBS), carboxylic anhydrides, especially phthalic anhydride, acylated polyhydric alcohols, especially triacetin, ethylene glycol diacetate, 2,5-diacetoxy-2,5-dihydrofuran, N-methylmorpholiniumacetonitrile methyl sulfate (MMA), and the enol esters known from German Patent Applications **DE 196 16 693** and **DE 196 16 767**, and also acetylated sorbitol and mannitol and/or mixtures thereof (SORMAN), acylated sugar derivatives, especially pentaacetylglucose (PAG), pentaacetylfructose, tetraacetylxylose and octaacetyllactose, and acetylated, optionally N-alkylated glucamine and gluconolactone, and/or N-acylated lactams, for example, N-benzoylcaprolactam. Hydrophilically substituted acylacetals and acyllactams are likewise used with preference. Combinations of conventional bleach activators may also be used. The bleach activators are used in machine dishwashing compositions usually in amounts of from 0.1 to 20% by weight, preferably from 0.25 to 15% by weight, and in particular from 1 to 10% by weight, based in each case on the composition. In the context of the present invention, the stated proportions relate to the weight of the base tablet.

In addition to the conventional bleach activators, or instead of them, it is also possible to incorporate what are known as bleaching catalysts into the rinse aid particles. These substances are bleach-boosting transition metal salts or transition metal complexes such as, for example, Mn-, Fe-, Co-, Ru- or Mo-salen complexes or -carbonyl complexes. Other bleaching catalysts which can be used include Mn, Fe, Co, Ru, Mo, Ti, V and Cu complexes with N-containing tripod ligands, and also Co-, Fe-, Cu- and Ru-ammine complexes.

Preference is given to the use of bleach activators from the group of polyacylated alkylenediamines,

especially tetraacetylethylenediamine (TAED), N-acyl imides, especially N-nonanoylsuccinimide (NOSI), acylated phenolsulfonates, especially n-nonanoyl- or isononanoyloxybenzenesulfonate (n- or iso-NOBS), N-methylmorpholiniumacetonitrile methyl sulfate (MMA), preferably in amounts of up to 10% by weight, in particular from 0.1% by weight to 8% by weight, more particularly from 2 to 8% by weight, and with particular preference from 2 to 6% by weight, based on the overall composition.

Bleach-boosting transition metal complexes, especially those with the central atoms Mn, Fe, Co, Cu, Mo, V, Ti and/or Ru, preferably selected from the group of manganese and/or cobalt salts and/or complexes, with particular preference from cobalt ammine complexes, cobalt acetato complexes, cobalt carbonyl complexes, the chlorides of cobalt or manganese, and manganese sulfate, are used in customary amounts, preferably in an amount of up to 5% by weight, in particular from 0.0025% by weight to 1% by weight, and with particular preference from 0.01% by weight to 0.25% by weight, based in each case on the overall composition. In specific cases, however, it is also possible to use a greater amount of bleach activator.

Laundry detergent and cleaning product tablets wherein the base tablet comprises bleaches from the group consisting of oxygen or halogen bleaches, especially chlorine bleaches, with particular preference sodium perborate and sodium percarbonate, in amounts of from 2 to 25% by weight, preferably from 5 to 20% by weight, and in particular from 10 to 15% by weight, based in each case on the weight of the base tablet, are a preferred embodiment of the present invention.

It is likewise preferred for the base tablet and/or the depression filling to comprise bleach activators.

Laundry detergent and cleaning product tablets wherein the base tablet comprises bleach activators from the groups of polyacylated alkylenediamines, especially tetraacetylethylenediamine (TAED), N-acyl imides, especially N-nonanoylsuccinimide (NOSI), acylated phenolsulfonates, especially n-nonanoyl- or isononanoyloxybenzenesulfonate (n- or iso-NOBS), and N-methylmorpholiniumacetonitrile methyl sulfate (MMA), in amounts of from 0.25 to 15% by weight, preferably from 0.5 to 10% by weight, and in particular from 1 to 5% by weight, based in each case on the weight of the base tablet, are likewise preferred.

The cleaning product tablets of the invention may include, especially in the base tablet, corrosion inhibitors for protecting the ware or the machine, with special importance in the field of machine dishwashing being possessed, in particular, by silver protectants. The known substances of the prior art may be used. In general it is possible to use, in particular, silver protectants selected from the group consisting of triazoles, benzotriazoles, bisbenzotriazoles, amino-triazoles, alkylaminotriazoles, and transition metal salts or transition metal complexes. Particular preference is given to the use of benzotriazole and/or alkylaminotriazole. Frequently encountered in cleaning formulations, furthermore, are agents containing active chlorine, which may significantly reduce corrosion of the silver surface. In chlorine-free cleaners, use is made in particular of oxygen-containing and nitrogen-containing organic redox-active compounds, such as divalent and trivalent phenols, e.g. hydroquinone, pyrocatechol, hydroxyhydroquinone, gallic acid, phloroglucinol, pyrogallol, and derivatives of these classes of compound. Inorganic compounds in the form of salts and complexes, such as salts of the metals Mn, Ti, Zr, Hf, V, Co and Ce, also find frequent application. Preference is given in this context to the

transition metal salts selected from the group consisting of manganese and/or cobalt salts and/or complexes, with particular preference cobalt ammine complexes, cobalt acetato complexes, cobalt carbonyl complexes, the chlorides of cobalt or of manganese and manganese sulfate. Similarly, zinc compounds may be used to prevent corrosion on the ware.

In laundry detergent and cleaning product tablets which are preferred in the context of the present invention, the base tablet comprises silver protectants from the group consisting of triazoles, benzotriazoles, bisbenzotriazoles, aminotriazoles, alkylaminotriazoles and the transition metal salts or transition metal complexes, with particular preference benzotriazole and/or alkylaminotriazole, in amounts of from 0.01 to 5% by weight, preferably from 0.05 to 4% by weight, and in particular from 0.5 to 3% by weight, based in each case on the weight of the base tablet.

Alternatively, of course, the depression filling may comprise silver protectants, in which case the base tablet either likewise comprises silver protectants or is free of such compounds.

In addition to the abovementioned ingredients, further classes of substance are suitable for incorporation into laundry detergents and cleaning products. Thus, preferred laundry detergent and cleaning product tablets are those wherein the base tablet further comprises one or more substances from the groups consisting of enzymes, corrosion inhibitors, scale inhibitors, cobuilders, dyes and/or fragrances in total amounts of from 6 to 30% by weight, preferably from 7.5 to 25% by weight, and in particular from 10 to 20% by weight, based in each case on the weight of the base tablet.

Suitable enzymes in the base tablets include in particular those from the classes of the hydrolases such as the proteases, esterases, lipases or lipolytic enzymes, amylases, glycosyl hydrolases, and mixtures of said enzymes. All of these hydrolases contribute to removing stains, such as proteinaceous, fatty or starchy marks. For bleaching, it is also possible to use oxidoreductases. Especially suitable enzymatic active substances are those obtained from bacterial strains or fungi such as Bacillus subtilis, Bacillus licheniformis, Streptomyces griseus, Coprinus cinereus and Humicola insolens, and also from genetically modified variants thereof. Preference is given to the use of proteases of the subtilisin type, and especially to proteases obtained from Bacillus lentus. Of particular interest in this context are enzyme mixtures, examples being those of protease and amylase or protease and lipase or lipolytic enzymes, or of protease, amylase and lipase or lipolytic enzymes, or protease, lipase or lipolytic enzymes, but especially protease and/or lipase-containing mixtures or mixtures with lipolytic enzymes. Examples of such lipolytic enzymes are the known cutinases. Peroxidases or oxidases have also proven suitable in some cases. The suitable amylases include, in particular, alpha-amylases, iso-amylases, pullulanases, and pectinases.

The enzymes may be adsorbed on carrier substances or embedded in sheathing substances in order to protect them against premature decomposition. The proportion of the enzymes, enzyme mixtures or enzyme granules may be, for example, from about 0.1 to 5% by weight, preferably from 0.5 to about 4.5% by weight. In cleaning product tablets which are preferred in the context of the present invention, the base tablet comprises protease and/or amylase.

By virtue of the fact that the laundry detergent and cleaning product tablets of the invention may contain the enzyme or enzymes in two regions which are different in principle, it is possible to provide tablets having very precisely defined enzyme release and enzyme activity. The table below gives an overview of possible enzyme distributions in laundry detergent and cleaning product tablets of the invention:

Base tablet	**Impressed depression filling**
Amylase	-
Protease	-
Lipase	-
Amylase + protease	-
Amylase + lipase	-
Protease + lipase	-
Amylase + protease + lipase	-
-	Amylase
-	Protease
-	Lipase
-	Amylase + protease
-	Amylase + lipase
-	Protease + lipase
-	Amylase + protease + lipase
Amylase	Amylase
Protease	Amylase
Amylase + protease	Amylase
Amylase	Protease
Protease	Protease
Amylase + protease	Protease
Amylase	Amylase + protease
Protease	Amylase + protease
Amylase + protease	Amylase + protease
Lipase	Amylase
Amylase + lipase	Amylase

Protease + lipase	Amylase
Amylase + protease + lipase	Amylase
Lipase	Protease
Amylase + lipase	Protease
Protease + lipase	Protease
Amylase + protease + lipase	Protease
Lipase	Amylase + protease
Amylase + lipase	Amylase + protease
Protease + lipase	Amylase + protease
Amylase + protease + lipase	Amylase + protease

Dyes and fragrances may be added to the machine dishwashing compositions of the invention both in the base tablet and in the depression filling region, in order to enhance the esthetic appeal of the products which are formed and to provide the consumer with not only the performance but also a visually and sensorially "typical and unmistakeable" product. As perfume oils and/or fragrances it is possible to use individual odorant compounds, examples being the synthetic products of the ester, ether, aldehyde, ketone, alcohol, and hydrocarbon types. Odorant compounds of the ester type are, for example, benzyl acetate, phenoxyethyl isobutyrate, p-tert-butyl-cyclohexyl acetate, linalyl acetate, dimethyl-benzylcarbinyl acetate, phenylethyl acetate, linalyl benzoate, benzyl formate, ethyl methylphenylglycinate, allyl cyclo-hexylpropionate, styrallyl propionate, and benzyl salicylate. The ethers include, for example, benzyl ethyl ether; the aldehydes include, for example, the linear alkanals having 8-18 carbon atoms, citral, citronellal, citronellyloxyacetaldehyde, cyclamen aldehyde, hydroxycitronellal, lilial and bourgeonal; the ketones include, for example, the ionones, α-isomethylionone and methyl cedryl ketone; the alcohols include anethole, citronellol, eugenol, geraniol, linalool, phenylethyl alcohol, and terpineol;

the hydrocarbons include primarily the terpenes such as limonenes and pinene. Preference, however, is given to the use of mixtures of different odorants, which together produce an appealing fragrance note. Such perfume oils may also contain natural odorant mixtures, as obtainable from plant sources, examples being pine oil, citrus oil, jasmine oil, patchouli oil, rose oil or ylang-ylang oil. Likewise suitable are clary sage oil, camomile oil, clove oil, balm oil, mint oil, cinnamon leaf oil, lime blossom oil, juniperberry oil, vetiver oil, olibanum oil, galbanum oil and labdanum oil, and also orange blossom oil, neroliol, orange peel oil, and sandalwood oil.

The fragrances may be incorporated directly into the laundry detergent and cleaning products of the invention; alternatively, it may be advantageous to apply the fragrances to carriers which intensify the adhesion of the perfume on the laundry and, by means of slower fragrance release, ensure long-lasting fragrance of the textiles. Materials which have become established as such carriers are, for example, cyclodextrins, it being possible in addition for the cyclodextrin-perfume complexes to be additionally coated with further auxiliaries.

In order to enhance the esthetic appeal of the composition of the invention, it (or parts thereof) may be colored with appropriate dyes. Preferred dyes, whose selection presents no difficulty whatsoever to the skilled worker, possess a high level of storage stability and insensitivity to the other ingredients of the compositions or to light and possess no pronounced affinity for the substrates to be treated with the compositions, such as textiles, glass, ceramic, or plastic tableware, so as not to stain them.

The above-described ingredients may of course also be incorporated into the depression filling. In laundry detergent and cleaning product tablets which are preferred in the context of the present invention, the part impressed into the base tablet comprises at least one active substance from the group consisting of enzymes, surfactants, soil release polymers, disintegration aids, bleaches, bleach activators, bleaching catalysts, silver protectants, and mixtures thereof.

By virtue of the division of the laundry detergent and cleaning product tablets of the invention into base tablet and impressed depression filling(s), it is possible to separate ingredients from one another; this may be utilized either for storage-stability-improving separation of incompatible ingredients or for controlled release of certain active substances. In preferred laundry detergent and cleaning product tablets, the base tablet or the part impressed into the base tablet comprises bleaches while the other part comprises bleach activators.

In further-preferred laundry detergent and cleaning product tablets, the base tablet or the part impressed into the base tablet comprises bleaches while the other part comprises enzymes.

Separation of bleach and corrosion inhibitors or silver protectants may also be realized. Laundry detergent and cleaning product tablets in which the base tablet or the part impressed into the base tablet comprises bleaches while the other part comprises corrosion inhibitors are likewise preferred.

Preference is also given not least to laundry detergent and cleaning product tablets wherein the base tablet or the part impressed into the base tablet comprises

bleaches while the other part comprises surfactants, preferably nonionic surfactants, with particular preference alkoxylated alcohols having 10 to 24 carbon atoms and from 1 to 5 alkylene oxide units.

Particularly preferred particulate compositions for impression into the depression tablets are those comprising surfactants, it being preferred to provide these surfactants in dissolution-retarded form in order to delay release of the impressed depression filling until the rinsing operation. Established for this purpose are, in particular, rinse aid particles as are described in the earlier German Patent Application **DE 199 14 364.1** (Henkel KGaA). Such particles, particularly preferred for impression into the depression, consist of from 30 to 90% by weight of one or more carrier materials, from 5 to 40% by weight of one or more coating substances having a melting point of more than 30°C, from 5 to 40% by weight of one or more active substances, and from 0 to 10% by weight of further active and auxiliary substances. The disclosure content of that document is expressly incorporated by reference. Nevertheless, the principal ingredients of these rinse aid particles which can be impressed with preference into the depression are described below. Suitable carrier substances a) are all substances which are solid at room temperature. Normally, the substances selected will be those which develop an additional action in the cleaning operation, builders being particularly appropriate. In preferred particulate rinse aids for the depression filling, the carrier materials present comprise substances from the group consisting of water-soluble laundry detergent and cleaning product ingredients, preferably carbonates, hydrogen carbonates, sulfates, phosphates, and organic oligocarboxylic acids which are solid at room temperature, in amounts of from 55 to 85% by weight, preferably from 60 to 80% by weight, and in particular

from 65 to 75% by weight, based in each case on the particle weight.

The abovementioned preferred carrier materials have already been described at length earlier on above.

The coating substances used in the rinse aid particles used preferably in accordance with the invention as the depression filling are subject to a variety of requirements, relating on the one hand to the melting behavior or, respectively, solidification behavior but on the other hand also to the material properties of the coating in the solidified state, i.e., in the rinse aid particles. Since the rinse aid particles are to be durably protected against ambient influences in transit or storage, the coating substance must possess a high stability with respect, for example, to impacts occurring in the course of packaging or transport. The coating substance should, therefore, have either at least partially elastic or at least plastic properties, in order to react by elastic or plastic deformation to any impact that does occur, and not to become crushed. The coating substance should have a melting range (solidification range) situated within a temperature range in which the active substances to be coated are not exposed to any excessive thermal load. On the other hand, however, the melting range must be sufficiently high still to offer effective protection for the active materials it encloses at at least slightly elevated temperature. In accordance with the invention, the coating substances have a melting point above 30°C.

It has proven advantageous for the coating substance not to exhibit a sharply defined melting point, as encountered commonly with pure, crystalline substances, but instead to have a melting range which covers, in some cases, several degrees Celsius.

The coating substance preferably has a melting range which lies between about 45°C and above 75°C. In the present case that means that the melting range occurs within the stated temperature interval, and does not denote the width of the melting range. The width of the melting range is preferably at least 1°C, more preferably from about 2 to about 3°C.

The abovementioned properties are in general possessed by what are called waxes. The term "waxes" is applied to a range of natural or synthetic substances which melt without decomposition, generally at above 40°C, and are of comparatively low viscosity, without stringing, at just a little above the melting point. They have a highly temperature-dependent consistency and solubility.

According to their origin, the waxes are divided into three groups: the natural waxes, chemically modified waxes, and the synthetic waxes.

The natural waxes include, for example, plant waxes such as candelilla wax, carnauba wax, japan wax, esparto grass wax, cork wax, guaruma wax, rice germ oil wax, sugarcane wax, ouricury wax, or montan wax, animal waxes such as beeswax, shellac wax, spermaceti, lanolin (wool wax), uropygial grease, mineral waxes such as ceresin or ozokerite (earth wax), or petrochemical waxes such as petrolatum, paraffin waxes or microcrystalline waxes.

The chemically modified waxes include, for example, hard waxes such as montan ester waxes, sassol waxes, or hydrogenated jojoba waxes.

By synthetic waxes are meant, in general, polyalkylene waxes or polyalkylene glycol waxes. As coating materials it is also possible to use compounds from

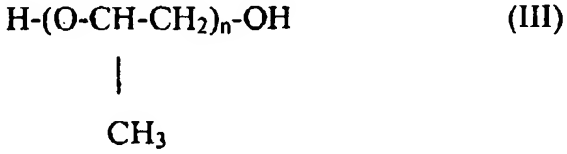
other classes of substance which meet the stated requirements in terms of softening point. Examples of synthetic compounds which have proven suitable are higher esters of phthalic acid, especially dicyclohexyl phthalate, which is available commercially under the name Unimoll® 66 (Bayer AG). Also suitable are synthetically prepared waxes from lower carboxylic acids and fatty alcohols, an example being dimyristyl tartrate, which is available under the name Cosmacol® ETLP (Condea). Conversely, synthetic or partially synthetic esters of lower alcohols with fatty acids from natural sources may also be used. This class of substance includes, for example, Tegin® 90 (Goldschmidt), a glyceryl monostearate palmitate. Shellac as well, for example, Schellack-KPS-Dreiring-SP (Kalkhoff GmbH), may be used according to the invention as a coating material.

Likewise counted among the waxes in the context of the present invention are, for example, the so-called wax alcohols. Wax alcohols are relatively high molecular mass, water-insoluble fatty alcohols having in general from about 22 to 40 carbon atoms. The wax alcohols occur, for example, in the form of wax esters of relatively high molecular mass fatty acids (wax acids) as a principal constituent of many natural waxes. Examples of wax alcohols are lignoceryl alcohol (1-tetracosanol), cetyl alcohol, myristyl alcohol, and melissyl alcohol. The coating of the particulate solids coated in accordance with the invention may, if desired, also include wool wax alcohols, by which are meant triterpenoid and steroid alcohols, an example being lanolin, which is available under the commercial designation Argowax® (Pamentier & Co.), for example. Likewise possible for use, at least proportionally, as a constituent of the coating are, in the context of the present invention, fatty acid glycerol esters or fatty acid alkanolamides, and also, if desired, water-

insoluble or only sparingly water-soluble polyalkylene glycol compounds.

Particularly preferred coating substances in the rinse aid particles for impression into the depression are those from the group consisting of polyethylene glycols (PEG) and/or polypropylene glycols (PPG), preference being given to polyethylene glycols having molecular masses of between 1500 and 36,000, particular preference to those having molecular masses of from 2000 to 6000, and special preference to those having molecular masses of from 3000 to 5000.

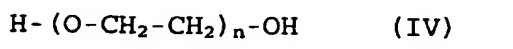
In this context, particularly preferred rinse aid particles are those comprising polypropylene glycols (PPG) and/or polyethylene glycols (PEG) as sole coating substance. Polypropylene glycols (abbreviation PPG) which may be used in accordance with the invention are polymers of propylene glycol which satisfy the general formula III



(III)

where n can adopt values between 10 and 2000. Preferred PPGs have molecular masses of between 1000 and 10,000 and, correspondingly, values of n of between 17 and approximately 170.

Polyethylene glycols (abbreviation PEG) which may be used with preference in accordance with the invention are polymers of ethylene glycol which satisfy the general formula IV



(IV)

where n can adopt values between 20 and approximately 1000. The abovementioned preferred molecular weight ranges correspond in this case to preferred ranges for the value n in formula IV of from about 30 to about 820 (to be exact: from 34 to 818), with particular preference from about 40 to about 150 (to be exact: from 45 to 136), and in particular from about 70 to about 120 (to be exact: from 68 to 113).

Preferably, the coating substance present in the rinse aid particles of the invention comprises paraffin wax in the predominant fraction. That means that at least 50% by weight of the total coating substances present, preferably more, consist of paraffin wax. Particularly suitable are paraffin wax contents (based on total coating substance) of approximately 60% by weight, approximately 70% by weight or approximately 80% by weight, with special preference being given to even higher proportions, of, for example, more than 90% by weight. In one particular embodiment of the invention, the total amount of the coating substance used consists exclusively of paraffin wax.

Relative to the other, natural waxes mentioned, paraffin waxes have the advantage in the context of the present invention that in an alkaline cleaning product environment there is no hydrolysis of the waxes (as is to be expected, for example, with the wax esters), since paraffin wax contains no hydrolyzable groups.

Paraffin waxes consist primarily of alkanes, plus low fractions of isoalkanes and cylcoalkanes. The paraffin for use in accordance with the invention preferably contains essentially no constituents having a melting point of more than 70°C, with particular preference of more than 60°C. Below this melting temperature in the cleaning product liquor, fractions of high-melting alkanes in the paraffin may leave unwanted wax residues

on the surfaces to be cleaned or on the ware to be cleaned. Wax residues of this kind lead in general to an unattractive appearance of the cleaned surface and should therefore be avoided.

Particulate rinse aids which may be impressed with preference into the depression comprise as coating substance at least one paraffin wax having a melting range from 50°C to 60°C.

Preferably, the amount of alkanes, isoalkanes and cycloalkanes which are solid at ambient temperature (from about 10 to about 30°C) in the paraffin wax used is as high as possible. The larger the amount of solid wax constituents in a wax at room temperature, the more useful that wax is in the context of the present invention. As the proportion of solid wax constituents increases, there is an increase in the resistance in the rinse aid particles to impacts or friction on other surfaces, resulting in a longer-lasting protection of the active substance particles. High proportions of oils or liquid wax constituents may weaken the particles, as a result of which pores are opened and the active substances are exposed to the ambient influences mentioned at the outset.

In addition to paraffin as main constituent, the coating substance may further comprise one or more of the abovementioned waxes or waxlike substances. In principle, the mixture forming the coated substance may be such that the rinse aid particles are at least substantially water-insoluble. At a temperature of about 30°C, the solubility in water should not exceed about 10 mg/l and preferably should be below 5 mg/l.

In any case, however, the coating should have as low a solubility in water as possible, even in water at elevated temperature, in order as far as possible to

avoid temperature-independent release of the active substances.

The principle described above is used for the delayed release of ingredients at a particular point in time in the cleaning operation and can be employed with particular advantage if rinsing is carried out in the main rinse cycle at a relatively low temperature (for example, 55°C), so that the active substance is not released from the rinse aid particles until the rinse cycle at higher temperatures (approximately 70°C).

Preferred particulate rinse aids which can be impressed into the depression, in accordance with the invention, comprise as coating substance one or more substances having a melting range of from 40°C to 75°C in amounts of from 6 to 30% by weight, preferably from 7.5 to 25% by weight, and in particular from 10 to 20% by weight, based in each case on the particle weight.

Active substance(s):

The active substances present in the rinse aid particles to be impressed into the depression, in accordance with the invention, may be present either in solid form or in liquid form at the processing temperature (i.e., at the temperature at which the particles are produced).

The active substances present in the rinse aid particles fulfill specific functions. By virtue of the separation of certain substances or of the temporally accelerated or delayed release of additional substances it is possible by this means to improve the cleaning performance. Active substances which are incorporated preferentially into the rinse aid particles are therefore laundry detergent and cleaning product ingredients which play a critical part in the washing or cleaning process.

Rinse aid particles to be incorporated preferably into the depression therefore comprise, as active substance, one or more substances from the groups consisting of surfactants, enzymes, bleaches, bleach activators, corrosion inhibitors, scale inhibitors, cobuilders and/or fragrances in amounts of from 60 to 30% by weight, preferably from 7.5 to 25% by weight, and in particular from 10 to 20% by weight, based in each case on the particle weight.

Through the incorporation of surfactants into melted coating material it is possible to prepare a melt suspension or melt emulsion which in the finished rinse aid particle and/or in the compressed tablet of the invention provides additional wash-active substance at a predeterminable point in time. For example, it is possible in this way to produce impressable rinse aid particles for machine dishwashing which release the additional surfactant from the tablet of the invention only at temperatures not attained by customary domestic dishwashing machines until the rinse cycle. Hence in the rinse cycle there is additional surfactant available which accelerates the runoff of the water and so effectively prevents marks on the ware. Given a suitable amount of solidified melt suspension or melt emulsion in the rinse aid particles, it is possible in this way to abandon the use of the additional rinse agents which are customary at present.

In rinse aid particles which can be impressed preferably into the depression, therefore, the active substance(s) is(are) selected from the group consisting of nonionic surfactants, especially alkoxylated alcohols. These substances have already been described at length.

Another class of active substances which can be incorporated with particular advantage into the rinse aid particles that can be impressed in accordance with the invention are bleaches. In this case it is possible to produce, and impress into the depression, particles which do not release the bleach until certain temperatures are reached; for example, ready-compounded detergents which clean enzymatically in the pre-rinse cycle and release the bleach only in the main rinse cycle. It is also possible to produce detergents for machine dishwashing in such a way that additional bleach is released in the rinse cycle so that difficult stains, for example, tea stains, are removed more effectively.

In particulate rinse aid particles which are impressed preferably into the depression, therefore, the active substance(s) is(are) selected from the group consisting of oxygen and halogen bleaches, especially chlorine bleaches. These substances have also already been described at length.

A further class of compounds which may be used with preference as active substances in the rinse aid particles that are impressed in accordance with the invention are the bleach activators. The important representatives from this group of substances have also been described already. In the context of the present invention, rinse aid particles impressed preferably into the depression comprise, as active substance, bleach activators, in particular from the groups consisting of polyacylated alkylenediamines, especially tetraacetylethylenediamine (TAED), N-acyl imides, especially N-nonanoylsuccinimide (NOSI), acylated phenolsulfonates, especially n-nonanoyl- or isononanoyloxybenzenesulfonate (n- or iso-NOBS), and N-methylmorpholiniumacetonitrile methyl sulfate (MMA).

A further important embodiment of the present invention envisages the impression of enzyme-containing rinse aid particles into the depression. Such rinse aid particles comprise as active substance(s) enzymes, which were described at length earlier on above. Particular preference is given in this context, as particles to be impressed into the depression, to those which comprise from 40 to 99.5% by weight, preferably from 50 to 97.5% by weight, with particular preference from 60 to 95% by weight, and in particular from 70 to 90% by weight, of one or more coating substances having a melting point of more than 30°C, from 0.5 to 60% by weight, preferably from 1 to 40% by weight, with particular preference from 2.5 to 30% by weight, and in particular from 5 to 25% by weight, of one or more liquid enzyme preparations dispersed in the coating substance(s), and from 0 to 20% by weight, preferably from 0 to 15% by weight, with particular preference from 0 to 10% by weight, and in particular from 0 to 5% by weight, optionally, of further carrier materials, auxiliary substances and/or active substances. The coating substances here are preferably polyethylene glycols and/or polypropylene glycols; as the active substances, liquid enzyme preparations have become established. Liquid enzyme concentrates of this kind are based either homogeneously on a propylene glycol/water base or heterogeneously in the form of a slurry, or are in microencapsulated structure. Preferred liquid proteases are, for example, Savinase® L, Durazym® L, Esperase® L, and Everlase® from Novo Nordisk, Optimase® L, Purafect® L, Purafect® OX L, Properase® L from Genencor International, and BLAP® L from Biozym Ges.m.b.H. Preferred amylases are Termamyl® L, Duramyl® L, and BAN® from Novo Nordisk, Maxamyl® WL and Purafect® HPAm L from Genencor International. Preferred lipases are Lipolase® L, Lipolase® ultra L and Lipoprime® L from Novo Nordisk and Lipomax® L from Genencor International.

As slurries or microencapsulated liquid products it is possible, for example, to use products such as the Novo Nordisk products designated with SL or LCC, respectively. These commercially customary liquid enzyme preparations contain, for example, from 20 to 90% by weight of propylene glycol or of mixtures of propylene glycol and water. In the context of the present invention, enzyme particles which can be impressed with preference into the depression comprise one or more liquid amylase preparations and/or one or more liquid protease preparations.

As active substances it is also possible to incorporate fragrances into the rinse aid particles to be impressed in accordance with the invention. All of the fragrances described at length earlier on above may be used as the active substance in this context. Incorporation of fragrances into the rinse aid particles results in detergents which release some or all of the fragrance with a time delay. In this way it is possible in accordance with the invention to produce, for example, machine dishwashing detergents with which the user experiences the perfume note even after the end of dishwashing, as the machine is opened. This makes it possible to eliminate the unwanted "alkali" odor which attaches to numerous machine dishwashing compositions.

Corrosion inhibitors as well may be incorporated as active substances into the rinse aid particles, in which case it is possible to use the substances familiar to the skilled worker. As a scale inhibitor, for example, it has become established to use a combination of enzyme (e.g., lipase) and lime soap dispersant.

Auxiliaries:

At extremely low temperatures, for example, at temperatures below 0°C, the rinse aid particles may be crushed on impact or friction or on being impressed into the depression. In order to improve the stability at such low temperatures, additives may if desired be admixed to the coating substances. Appropriate additives must be able to be mixed completely with the melted wax, must not significantly alter the melting range of the coating substances, must improve the elasticity of the coating at low temperatures, must not increase the permeability of the coating for water or moisture in general, and must not raise the viscosity of the melt of the coating material to an extent such that processing is hindered or even made impossible. Suitable additives which reduce at low temperatures the brittleness of a coating consisting essentially of paraffin are, for example, EVA copolymers, hydrogenated resin acid methyl esters, polyethylene, or copolymers of ethyl acrylate and 2-ethylhexyl acrylate.

A further judicious additive when using paraffin as the coating is a small amount of a surfactant, for example, a C_{12-18} fatty alcohol sulfate. Such an addition results in better wetting by the coating of the material to be embedded. The additive is added advantageously in an amount of approximately < 5% by weight, preferably < approximately 2% by weight, based on the coating substance. The addition of an additive may in many cases make it possible to coat even those active substances which without the addition of additive generally form a tough, plastic mass of paraffin and part-dissolved active substance after the coating material has melted.

It may also be of advantage to add further additives to the coating substance in order, for example, to prevent premature settling of the active substances. This is

particularly advisable when producing the rinse aid particles of the invention without carrier substances. The antisettling agents which can be used for this purpose, which are also referred to as suspension agents, are known from the prior art, for example, from the manufacture of paints and printing inks. In order to avoid sedimentation phenomena and concentration gradients of substances to be coated, on transition from the plastic solidification range to the solid, it is appropriate, for example, to use surface-active substances, solvent-dispersed waxes, montmorillonites, organically modified bentonites, (hydrogenated) castor oil derivatives, soya lecithin, ethylcellulose, low moelcular mass polyamides, metal stearates, calcium soaps, or hydrophobicized silicas. Further substances which bring about said effects originate from the groups of the antifloating agents and the thixotropic agents and may be designated chemically as silicone oils (dimethylpolysiloxanes, methylphenylpolysilixanes, polyether-modified methylalkylpolysiloxanes), oligomeric titanates and silanes, polyamines, salts of long-chain polyamines and polycarboxylic acids, amine/amide-functional polyesters, and amine/amide-functional polyacrylates.

Additives from said classes of substance are available commercially in pronounced diversity. Examples of commercial products which may be added advantageously as additives in the context of the present process are, for example, Aerosil® 200 (pyrogenic silica, Degussa), Bentone® SD-1, SD-2, 34, 52 and 57 (bentonite, Rheox), Bentone® SD-3, 27 and 38 (hectorite, Rheox), Tixogen® EZ 100 or VP-A (organically modified smectite, Südchemie), Tixogel® VG, VP and VZ (QAV-laden montmorillonite, Südchemie), Disperbyk® 161 (block copolymer, Byk-Chemie), Borchigen® ND (nonsulfo-group ion exchanger, Borchers), Ser-Ad® FA 601 (Servo), Solsperse® (aromatic ethoxylate, ICI), Surfynol® grades

(Air Products), Tamol® and Triton® grades (Rohm & Haas), Texaphor® 963, 3241 and 3250 (polymers, Henkel), Rilanit® grades (Henkel), Thixcin® E and R (castor oil derivatives, Rheox), Thixatrol® ST and GST (castor oil derivatives, Rheox), Thixatrol® SR, SR 100, TSR and TSR 100 (polyamide polymers, Rheox), Thixatrol® 289 (polyester polymer, Rheox), and the various M-P-A® grades X, 60-X, 1078-X, 2000-X and 60-MS (organic compounds, Rheox).

Depending on coating material and active substance, said auxiliaries may be used in varying amounts in the rinse aid particles to be impressed in accordance with the invention. Customary use concentrations for the abovementioned antisettling, antifloating, thixotropic and dispersing agents lie within the range from 0.5 to 8.0% by weight, preferably between 1.0 and 5.0% by weight, and with particular preference between 1.5 and 3.0% by weight, based in each case on the total amount of coating substance and active substances.

In the context of the present invention, particulate rinse aids to be impressed preferably into the depression comprise further auxiliaries from the group consisting of antisettling agents, suspension agents, antifloating agents, thixotropic agents and auxiliary dispersing agents in amounts of from 0.5 to 9% by weight, preferably between 1 and 7.5% by weight, and with particular preference between 1.5 and 5% by weight, based in each case on the particle weight.

Especially in the case of the preparation of melt suspensions and melt emulsions comprising active substances which are liquid at the processing temperature, the use of specific emulsifiers is advantageous. It has been found that emulsifiers from the group consisting of fatty alcohols, fatty acids, polyglycerol esters and polyoxyalkylenesiloxanes, in

particular, are extremely well suited. Further details on the production of the rinse aid particles of the invention follow later on below.

Fatty alcohols in this context are the alcohols having 6 to 22 carbon atoms that are obtainable from natural fats and oils via the corresponding fatty acids (see below). Depending on the origin of the fat or oil from which they are obtained, these alcohols may be substituted in the alkyl chain or unsaturated at certain points.

As emulsifiers in the rinse aid particles of the invention it is therefore preferred to use C_{6-22} fatty alcohols, preferably C_{8-22} fatty alcohols, and in particular C_{12-18} fatty alcohols, with particular preference the C_{16-18} fatty alcohols.

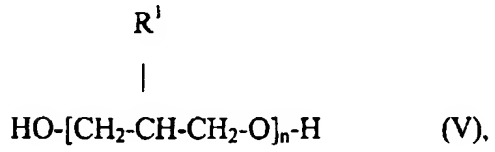
As emulsifiers it is also possible to use all fatty acids obtained from vegetable or animal oils and fats. Irrespective of their aggregate state, the fatty acids may be saturated or mono- to polyunsaturated. In the case of the unsaturated fatty acids as well, the species which are solid at room temperature are preferred over the liquid or pastelike species. Of course, it is possible to use not only "pure" fatty acids but also the fatty acid mixtures obtained in the course of cleavage from fats and oils, these mixtures being distinctly preferred in turn from an economic standpoint.

Consequently, as emulsifiers in the context of the present invention, it is possible to use, for example, individual species or mixtures of the following acids: caprylic acid, pelargonic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, octadecane-12-oleic acid, arachidic acid, behenic acid, lignoceric acid, cerotic acid, melissic acid,

10-undecenoic acid, petroselinic acid, petroselaidic acid, oleic acid, elaidic acid, ricinoleic acid, linolaidic acid, α- and β-eleostearic acid, gadoleic acid, erucic acid, brassidic acid. It is of course also possible to use the fatty acids having an odd number of carbon atoms, examples being undecanoic acid, tridecanoic acid, pentadecanoic acid, heptadecanoic acid, nonadecanoic acid, heneicosanoic acid, tricosanoic acid, pentacosanoic acid, heptacosanoic acid.

In preferred rinse aid particles the emulsifier(s) used comprise C_{6-22} fatty acids, preferably C_{8-22} fatty acids and in particular C_{12-18} fatty acids, with particular preference the C_{16-18} fatty acids.

Particularly preferred emulsifiers in the context of the present invention are polyglycerol esters, especially esters of fatty acids with polyglycerols. These preferred polyglycerol esters can be described by the general formula V

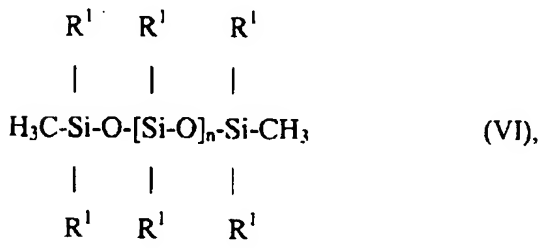


in which R^1 in each glycerol unit independently of one another is H or a fatty acyl radical having 8 to 22 carbon atoms, preferably having 12 to 18 carbon atoms, and n is a number between 2 and 15, preferably between 3 and 10.

These polyglycerol esters are known and commercially available in particular with the degrees of polymerization n = 2, 3, 4, 6 and 10. Since substances of the stated type also find broad application in cosmetic formulations, a considerable number of these

substances are also classified in the INCI nomenclature (CTFA International Cosmetic Ingredient Dictionary and Handbook, 5th edition, The Cosmetic, Toiletry and Fragrance Association, Washington, 1997). This standard work of cosmetology includes, for example, information under the headings POLYGLYCERYL-3 BEESWAX, POLYGLYCERYL-3 CETYL ETHER, POLYGLYCERYL-4 COCOATE, POLYGLYCERYL-10 DECALINOLEATE, POLYGLYCERYL-10 DECAOLEATE, POLYGLYCERYL-10 DECASTEARATE, POLYGLYCERYL-2 DIISOSTEARATE, POLYGLYCERYL-3 DIISOSTEARATE, POLYGLYCERYL-10 DIISOSTEARATE, POLYGLYCERYL-2 DIOLEATE, POLYGLYCERYL-3 DIOLEATE, POLYGLYCERYL-6 DIOLEATE, POLYGLYCERYL-10 DIOLEATE, POLYGLYCERYL-3 DISTEARATE, POLYGLYCERYL-6 DISTEARATE, POLYGLYCERYL-10 DISTEARATE, POLYGLYCERYL-10 HEPTAOLEATE, POLYGLYCERYL-12 HYDROXYSTEARATE, POLYGLYCERYL-10 HEPTASTEARATE, POLYGLYCERYL-6 HEXAOLEATE, POLYGLYCERYL-2 ISOSTEARATE, POLYGLYCERYL-4 ISOSTEARATE, POLYGLYCERYL-6 ISOSTEARATE, POLYGLYCERYL-10 LAURATE, POLYGLYCERYL METHACRYLATE, POLYGLYCERYL-10 MYRISTATE, POLYGLYCERYL-2 OLEATE, POLYGLYCERYL-3 OLEATE, POLYGLYCERYL-4 OLEATE, POLYGLYCERYL-6 OLEATE, POLYGLYCERYL-8 OLEATE, POLYGLYCERYL-10 OLEATE, POLYGLYCERYL-6 PENTAOLEATE, POLYGLYCERYL-10 PENTAOLEATE, POLYGLYCERYL-6 PENTASTEARATE, POLYGLYCERYL-10 PENTASTEARATE, POLYGLYCERYL-2 SESQUIISOSTEARATE, POLYGLYCERYL-2 SESQUIOLEATE, POLYGLYCERYL-2 STEARATE, POLYGLYCERYL-3 STEARATE, POLYGLYCERYL-4 STEARATE, POLYGLYCERYL-8 STEARATE, POLYGLYCERYL-10 STEARATE, POLYGLYCERYL-2 TETRAISOSTEARATE, POLYGLYCERYL-10 TETRAOLEATE, POLYGLYCERYL-2 TETRASTEARATE, POLYGLYCERYL-2 TRIISOSTEARATE, POLYGLYCERYL-10 TRIOLEATE, POLYGLYCERYL-6 TRISTEARATE. The commercially available products from various manufacturers, which are classified in said work under the above headings, may be used with advantage as emulsifiers in process step b) of the invention.

A further group of emulsifiers which may be used in the rinse aid particles of the invention are substituted silicones which carry side chains that have been reacted with ethylene oxide and/or propylene oxide. Such polyoxyalkylenesiloxanes may be described by the general formula VI



(VI),

in which each radical R^1 independently of one another is $-CH_3$ or a polyoxyethylene or polyoxypropylene group $-[CH(R^2)-CH_2-O]_xH$, R^2 is -H or $-CH_3$, x is a number between 1 and 100, preferably between 2 and 20, and in particular below 10, and n indicates the degree of polymerization of the silicone.

Optionally, said polyoxyalkylenesiloxanes may also be etherified or esterified on the free OH groups of the polyoxyethylene and/or polyoxypropylene side chains. The unetherified and unesterified polymer of dimethylsiloxane with polyoxyethylene and/or polyoxypropylene is referred to in the INCI nomenclature as DIMETHICONE COPOLYOL and is available commercially under the trade names Abil® B (Goldschmidt), Alkasil® (Rhône-Poulenc), Silwet® (Union Carbide) or Belsil® DMC 6031.

The acetic-acid-esterified DIMETHICONE COPOLYOL ACETATE (for example, Belsil® DMC 6032, -33 and -35, Wacker) and DIMETHICONE COPOLYOL BUTYL ETHER (e.g., KF352A, Shin Etsu) are likewise suitable for use as emulsifiers in the context of the present invention.

In the case of the emulsifiers, as already with the coating materials and the substances to be coated, it is the case that they may be used over a widely varying range. Normally, emulsifiers of the abovementioned type make up from 1 to 25% by weight, preferably from 2 to 20% by weight, and in particular from 5 to 10% by weight, of the weight of the sum of coating materials and active substances.

Particulate rinse aids to be impressed preferably into the depression in the context of the present invention further comprise emulsifiers from the group of fatty alcohols, fatty acids, polyglycerol esters and/or polyoxyalkylenesiloxanes in amounts from 0.1 to 5% by weight, preferably from 0.2 to 3.5% by weight, with particular preference from 0.5 to 2% by weight, and in particular from 0.75 to 1.25% by weight, based in each case on the particle weight.

The part to be impressed into the depression of the base tablet may be placed into the depression in the form of a particulate composition and converted there by impressing into a compact constituent of the tablet. In this context it is possible to make a free choice of such particulate compositions both in terms of their particle size and in terms of their bulk density and their genesis, i.e., the process used to produce them. In particular, therefore, it is possible to impress dusts, powders, granules, extrudates, compression agglomerates, compacts, flakes, flocs, etc. as particles into the depression, where they form the compressed part b) of the tablets of the invention.

When meltable substances are used as an ingredient of the compressed part b), it is possible to use other processes as well to prepare particulate preparations which are impressed into the depression, this being preferred in the context of the present invention.

Particularly suitable such processes include prilling, pelletizing or flaking.

The process preferably to be employed in accordance with the invention to produce compressible particles, which is referred to for short as prilling, comprises the production of granular elements from meltable substances, the melt comprising the respective ingredients being sprayed in in defined droplet size at the top of a tower, solidifying in free fall, and being obtained as prill granules at the base of the tower.

As the cold gas stream it is possible in very general terms to use all gases, the temperature of the gas being below the melting temperature of the melt. In order to avoid long falling sections, use is frequently made of cooled gases, for example, supercooled air or even liquid nitrogen, which is injected through a nozzle into the spray towers.

The particle size of the resulting prills may be varied by way of the choice of droplet size, with particle sizes which are easy to realize technically lying within the range from 0.5 to 2 mm, preferably around 1 mm.

An alternative process for prilling is pelletizing. A further embodiment of the present invention therefore envisages as a component step a process for producing pelletized cleaning product components in which a melt is metered onto cooled pelletizing plates.

Pelletizing comprises the metering of the melt comprising the respective ingredients onto a (cooled) belt or onto rotating, inclined plates which have a temperature below the melting temperature of the melt and are preferably cooled below room temperature. Here again, process variants may be practiced in which the

pelletizing plates are supercooled. In this case, however, measures must be taken to counter the condensation of atmospheric moisture.

Pelletizing produces relatively large particles, which in standard industrial processes have sizes of between 2 and 10 mm, preferably between 3 and 6 mm.

As an even more cost-effective variant for producing particulate cleaning product components of said composition from melts, the use of cooling rolls is appropriate. A further component step of the present invention is therefore a process for producing particulate cleaning product components in which a melt is applied by spraying or otherwise to a cooling roll, the solidified melt is stripped off, and the scrapings are, if necessary, comminuted. The use of cooling rolls permits ready establishment of the desired particle size range, which in this process may also be below 1 mm, for example from 200 to 700 μm.

Of course, it is also possible in accordance with the invention to compress the particulate compositions into a separate "core tablet" before impression into the depression. This "core tablet" can then be placed into the depression in the form of a "large, individual particle" and impressed. In this case the core tablet may be produced in such a way that it can be inserted directly into the depression, although its geometry may also be chosen such that the final positive fit with the impression is accomplished only by means of the impressing operation.

Especially when using meltable substances in the tablet part b), the production of the tablets of the invention by separate production (compressing) of a base tablet a) and a core tablet b), which is preferably pressed from prills, the joining and the final

compression of both parts, is preferred. In preferred embodiments of this process variant, the impressed tablet is multiphase.

It is not solely complete separation of the ingredients that may be advantageous; by means of varying amounts of individual ingredients in the different tablet regions it is also possible to achieve advantageous effects. Laundry detergent and cleaning product tablets wherein the base tablet and the part impressed into the base tablet contain the same active substance in different amounts are preferred in accordance with the invention. Examples of ingredients where there are advantages to division into the different regions are disintegration aids, dyes and fragrances, optical brighteners, polymers, silver protectants, surfactants, and enzymes. The phrase "different amounts" denotes the amount of the substance in question in the individual tablet region, based on the tablet region, and is therefore a percentage by weight which does not relate to the absolute amounts of the ingredient.

Laundry detergent and cleaning product tablets which are preferred in the context of the present invention are those wherein the tablets comprise less than 2% by weight, preferably less than 1.5% by weight, with particular preference less than 1% by weight, and in particular less than 0.5% by weight, of free water. The term "free water" denotes the water content of the composition which is not bonded in the form of hydrate water and/or constitution water. In preferred laundry detergent and cleaning product tablets said content is below 2% by weight, preferably below 1.5% by weight, with particular preference below 1% by weight, and in particular even below 0.5% by weight, based in each case on the composition. Water may accordingly be present essentially only in chemically and/or physically bound form or as a constituent of the solid

raw materials or compounds, but not as a liquid, solvent or dispersion in the laundry detergent and cleaning product tablets of the invention. Advantageously, the laundry detergent and cleaning product tablets of the invention have an overall water content of not more than 15% by weight, with this water, therefore, being present not in liquid, free form but instead in chemically and/or physically bound form, and it being particularly preferred for the amount of water in the compositions of the invention that is not bound to carbonates and/or to silicates to amount to not more than 10% by weight and in particular not more than 7% by weight. In the production of the compositions of the invention it is possible to use liquids which contain water provided that by adding an "internal siccative", for example, a hydratable substance in unhydrated form, the amount of free water is held below the stated limit.

The part impressed into the base tablet is already adhered firmly to the surface of the base tablet as a result of the application of the compressive pressure in the production operation. In order to bring about further stabilization for extreme loads or to effect protection of the depression filling against atmospheric effects, a coating may be applied to the depression filling or to tablet sides which carry the depression filling. Laundry detergent and cleaning product tablets wherein the part impressed into the base tablet is coated with a coating layer are preferred in accordance with the invention.

Of course, the whole tablet may also be coated with a coating layer.

The laundry detergent and cleaning product tablets of the invention dissolve completely in the washing or cleaning operation, it being possibly advantageous - as

mentioned above - for the different regions to have different dissolution rates. By dint of the different dissolution rates, it is possible not only to release certain ingredients at certain points in time but also to tailor the properties of the washing or cleaning liquor. For example, preference is given to laundry detergent and cleaning product tablets wherein the pH of a 1% strength solution of the base tablet in water is in the range from 8 to 12, preferably from 9 to 11, and in particular from 9.5 to 10.

In addition, preference is given to laundry detergent and cleaning product tablets wherein the pH of a 1% strength solution of the entire tablet in water is in the range from 7 to 11, preferably from 7.5 to 10, and in particular from 8 to 9.5.

The present invention further comprises a process for producing laundry detergent and cleaning product tablets, which comprises the steps of

a) compressing a particulate premix to form a compressed part (base tablet) which has at least one depression,
b) filling one or more particulate composition(s) into said depression(s),
c) compressing the composition(s) filled in in step b) to form (a) further compressed part(s) which is/are present in impressed form in said depression(s) of the base tablet, and
d) optionally aftertreating individual tablet areas or the entire tablet.

Regarding the ingredients of the individual particulate premixes or compositions which result in the different regions of the tablet, the comments made above for the tablets of the invention apply analogously.

It has proven advantageous if the premix compressed in step a) to form base tablets satisfies certain physical criteria. Preferred processes are, for example, those wherein the particulate premix in step a) has a bulk density of at least 500 g/l, preferably at least 600 g/l, and in particular at least 700 g/l.

The particle size of the premix compressed in step a) also preferably satisfies certain criteria: processes wherein the particulate premix in step a) has particle sizes of between 100 and 2000 μm, preferably between 200 and 1800 μm, with particular preference between 400 and 1600 μm, and in particular between 600 and 1400 μm, are preferred in accordance with the invention. A further-narrowed particle size in the premixes intended for compression may be established in order to obtain advantageous tablet properties. In preferred variants of the process of the invention, the particulate premix compressed in step a) has a particle size distribution in which less than 10% by weight, preferably less than 7.5% by weight, and in particular less than 5% by weight, of the particles are greater than 1600 μm or smaller than 200 μm. Narrower particle size distributions are further preferred in this context. In particularly advantageous process variants, the particulate premix compressed in step a) has a particle size distribution in which more than 30% by weight, preferably more than 40% by weight, and in particular more than 50% by weight, of the particles have a size of between 600 and 1000 μm.

In connection with the implementation of step a), the process of the invention is not restricted to compressing only one particulate premix to form a tablet. Rather, step a) of the process may also be extended to the effect that, in a manner known per se, multilayer tablets are produced by preparing two or more premixes which are compressed one atop another. In

this case, the first premix filled in is slightly precompressed in order to acquire a smooth top face which extends parallel to the tablet body, and, after the second premix has been filled in, final compression takes place to form the finished tablet. In the case of tablets with three or more layers there is a further precompression following the addition of each premix before the tablet, after the addition of the last premix, undergoes final compression. Preferably, the above-described cavity in the base tablet is a depression, so that in preferred embodiments of the first process of the invention, in step a), multilayer tablets having a depression are produced in a manner known per se by compressing a plurality of different particulate premixes one atop another.

The tablets of the invention are produced in step a) first of all by dry-mixing the constituents, some or all of which may have been pregranulated, and subsequently shaping the dry mixture, in particular by compression to tablets, in which context it is possible to have recourse to conventional processes. To produce the tablets of the invention, the premix is compacted in a so-called die between two punches to form a solid compact. This operation, which is referred to below for short as tableting, is divided into four sections: metering, compaction (elastic deformation), plastic deformation, and ejection.

First of all, the premix is introduced into the die, the fill level and thus the weight and form of the resulting tablet being determined by the position of the lower punch and by the form of the compression tool. Even in the case of high tablet throughputs, constant metering is preferably achieved by volumetric metering of the premix. In the subsequent course of tableting, the upper punch contacts the premix and is lowered further in the direction of the lower punch. In

the course of this compaction the particles of the premix are pressed closer to one another, with a continual reduction in the void volume within the filling between the punches. When the upper punch reaches a certain position (and thus when a certain pressure is acting on the premix), plastic deformation begins, in which the particles coalesce and the tablet is formed. Depending on the physical properties of the premix, a portion of the premix particles is also crushed and at even higher pressures there is sintering of the premix. With an increasing compression rate, i.e., high throughputs, the phase of elastic deformation becomes shorter and shorter, with the result that the tablets formed may have larger or smaller voids. In the final step of tableting, the finished tablet is ejected from the die by the lower punch and conveyed away by means of downstream transport means. At this point in time, it is only the weight of the tablet which has been ultimately defined, since the compacts may still change their form and size as a result of physical processes (elastic relaxation, crystallographic effects, cooling, etc).

Tableting takes place in commercially customary tableting presses, which may in principle be equipped with single or double punches. In the latter case, pressure is built up not only using the upper punch; the lower punch as well moves toward the upper punch during the compression operation, while the upper punch presses downward. For small production volumes it is preferred to use eccentric tableting presses, in which the punch or punches is or are attached to an eccentric disk, which in turn is mounted on an axle having a defined speed of rotation. The movement of these compression punches is comparable with the way in which a customary four-stroke engine works. Compression can take place with one upper and one lower punch, or else a plurality of punches may be attached to one eccentric

disk, the number of die bores being increased correspondingly. The throughputs of eccentric presses vary, depending on model, from several hundred up to a maximum of 3000 tablets per hour.

For greater throughputs, the apparatus chosen comprises rotary tableting presses, in which a relatively large number of dies is arranged in a circle on a so-called die table. Depending on model, the number of dies varies between 6 and 55, larger dies also being obtainable commercially. Each die on the die table is allocated an upper punch and a lower punch, it being possible again for the compressive pressure to be built up actively by the upper punch or lower punch only or else by both punches. The die table and the punches move around a common, vertical axis, and during rotation the punches, by means of raillike cam tracks, are brought into the positions for filling, compaction, plastic deformation, and ejection. At those sites where considerable raising or lowering of the punches is necessary (filling, compaction, ejection), these cam tracks are assisted by additional low-pressure sections, low tension rails, and discharge tracks. The die is filled by way of a rigid supply means, known as the filling shoe, which is connected to a stock vessel for the premix. The compressive pressure on the premix can be adjusted individually for upper punch and lower punch by way of the compression paths, the buildup of pressure taking place by the rolling movement of the punch shaft heads past displaceable pressure rolls.

In order to increase the throughput, rotary presses may also be provided with two filling shoes, in which case only one half-circle need be traveled to produce one tablet. For the production of two-layer and multilayer tablets, a plurality of filling shoes are arranged in series, and the gently pressed first layer is not ejected before further filling. By means of an

appropriate process regime it is possible in this way to produce laminated tablets and inlay tablets as well, having a construction like that of an onion skin, where in the case of the inlay tablet the top face of the core or of the core layers is not covered and therefore remains visible. Rotary tableting presses can also be equipped with single or multiple tools, so that, for example, an outer circle with 50 bores and an inner circle with 35 bores can be used simultaneously for compresssion. The throughputs of modern rotary tableting presses amount to more than a million tablets per hour.

When tableting with rotary presses it has been found advantageous to perform tableting with minimal fluctuations in tablet weight. Fluctuations in tablet hardness can also be reduced in this way. Slight fluctuations in weight can be achieved as follows:

- use of plastic inserts with small thickness tolerances
- low rotor speed
- large filling shoes
- harmonization between the filling shoe wing rotary speed and the speed of the rotor
- filling shoe with constant powder height
- decoupling of filling shoe and powder charge

To reduce caking on the punches, all of the antiadhesion coatings known from the art are available. Polymer coatings, plastic inserts or plastic punches are particularly advantageous. Rotating punches have also been found advantageous, in which case, where possible, upper punch and lower punch should be of rotatable configuration. In the case of rotating punches, it is generally possible to do without a plastic insert. In this case the punch surfaces should be electropolished.

It has also been found that long compression times are advantageous. These times can be established using pressure rails, a plurality of pressure rolls, or low rotor speeds. Since the fluctuations in tablet hardness are caused by the fluctuations in the compressive forces, systems should be employed which limit the compressive force. In this case it is possible to use elastic punches, pneumatic compensators, or sprung elements in the force path. In addition, the pressure roll may be of sprung design.

Tableting machines suitable in the context of the present invention are obtainable, for example, from the following companies: Apparatebau Holzwarth GbR, Asperg, Wilhelm Fette GmbH, Schwarzenbek, Hofer GmbH, Weil, Horn & Noack Pharmatechnik GmbH, Worms, IMA Verpackungssysteme GmbH, Viersen, KILIAN, Cologne, KOMAGE, Kell am See, KORSCH Pressen AG, Berlin, and Romaco GmbH, Worms. Examples of further suppliers are Dr. Herbert Pete, Vienna (AU), Mapag Maschinenbau AG, Berne (CH), BWI Manesty, Liverpool (GB), I. Holland Ltd., Nottingham (GB), Courtoy N.V., Halle (BE/LU), and Medicopharm, Kamnik (SI). A particularly suitable apparatus is, for example, the hydraulic double-pressure press HPF 630 from LAEIS, D. Tableting tools are obtainable, for example, from the following companies: Adams Tablettierwerkzeuge, Dresden, Wilhelm Fett GmbH, Schwarzenbek, Klaus Hammer, Solingen, Herber & Söhne GmbH, Hamburg, Hofer GmbH, Weil, Horn & Noack, Pharmatechnik GmbH, Worms, Ritter Pharmatechnik GmbH, Hamburg, Romaco GmbH, Worms, and Notter Werkzeugbau, Tamm. Further suppliers are, for example, Senss AG, Reinach (CH) and Medicopharm, Kamnik (SI).

The tablets can be produced - as already mentioned earlier above - in predetermined three-dimensional forms and predetermined sizes. Suitable three-dimensional forms are virtually any practicable designs

- i.e., for example, bar, rod or ingot form, cubes, blocks and corresponding three-dimensional elements having planar side faces, and in particular cylindrical designs with a circular or oval cross section. This latter design covers forms ranging from tablets through to compact cylinders having a height-to-diameter ratio of more than 1.

Another preferred tablet which can be produced has a platelike or barlike structure with, in alternation, long, thick and short, thin segments, so that individual segments can be broken off from this "slab" at the predetermined breaking points, represented by the short, thin segments, and inserted into the machine. This principle of the "slablike" tablet detergent may also be realized in other geometric forms; for example, vertical triangles connected to one another lengthwise at only one of their sides.

However, it is also possible for the various components not to be compressed to a homogeneous tablet, but instead to obtain tablets having a plurality of layers, i.e., at least two layers. In this case it is also possible for these different layers to have different dissolution rates. This may result in advantageous performance properties for the tablets. If, for example, there are components present in the tablets which have adverse effects on each other, then it is possible to integrate one component into the quicker-dissolving layer and the other component into a slower-dissolving layer, so that the first component has already reacted when the second passes into solution. The layer structure of the tablets may be realized in stack form, in which case dissolution of the inner layer(s) at the edges of the tablet takes place at a point when the outer layers have not yet fully dissolved; alternatively, the inner layer(s) may also be completely enveloped by the respective outerlying

layer(s), which prevents premature dissolution of constituents of the inner layer(s).

In one further-preferred embodiment of the invention, a tablet consists of at least three layers, i.e., two outer and at least one inner layer, with at least one of the inner layers comprising a peroxy bleach, while in the stack-form tablet the two outer layers, and in the case of the envelope-form tablet the outermost layers, are free from peroxy bleach. Furthermore, it is also possible to provide spatial separation of peroxy bleach and any bleach activators and/or enzymes present in a tablet. Multilayer tablets of this kind have the advantage that they can be used not only by way of a dispenser drawer or by way of a metering device which is placed into the washing liquor; instead, in such cases it is also possible to place the tablet into the machine in direct contact with the textiles without fear of spotting by bleaches and the like.

Similar effects can also be achieved by coating individual constituents of the laundry detergent and cleaning product composition intended for compression, or of the tablet as a whole. For this purpose the elements to be coated may be sprayed, for example, with aqueous solutions or emulsions, or else a coating may be obtained by the technique of melt coating.

After compression, the laundry detergent and cleaning product tablets possess high stability. The fracture strength of cylindrical tablets can be gaged by way of the parameter of diametral fracture stress. This diametral fracture stress can be determined by

$$\sigma = \frac{2P}{\pi Dt}$$

where σ represents the diametral fracture stress (DFS) in Pa, P is the force in N which leads to the pressure exerted on the tablet, which pressure causes the fracture of the tablet, D is the tablet diameter in meters, and t is the tablet height.

The depression tablets are filled in step b) with a pulverulent composition, which in step c) is impressed into the tablet. In analogy to the details given for process step a), it is also possible to specify preferred physical parameters for the particulate composition(s) in process step b): processes wherein the particulate composition(s) in step b) has/have a bulk density of at least 500 g/l, preferably at least 600 g/l, and in particular at least 700 g/l, and processes wherein the particulate composition(s) in step b) has/have particle sizes of between 100 and 2000 μm, preferably between 200 and 1800 μm, with particular preference between 400 and 1600 μm, and in particular between 600 and 1400 μm, are preferred embodiments of the present invention.

The compressive force which acts on the base tablet and on the depression filling, respectively, in steps a) and b) during compression leads preferably to different loads per unit area, i.e., compressive pressures. Processes wherein compression in step a) takes place at compressive pressures of from 0.01 to 50 kN cm^{-2}, preferably from 0.1 to 40 kN cm^{-2}, and in particular from 1 to 25 kN cm^{-2}, and processes wherein compression in step c) takes place at compressive pressures of from 1 to 100 kN cm^{-2}, preferably from 2.5 to 50 kN cm^{-2}, and in particular from 5 to 25 kN cm^{-2}, are preferred in accordance with the invention.

The compression of the particulate composition into the depression may take place in analogy to the production of the base tablets on tableting presses. Preference is

given to a procedure in which first the base tablet including depression is produced, then filling is carried out, and subsequently compression is repeated. This can be done by ejecting the base tablets from a first tableting press, filling them, and transporting them into a second tableting press in which final compression takes place. Alternatively, final compression may also take place by means of pressure rolls which roll over the tablets situated on a conveyor belt. Yet another possibility is to provide a rotary tableting press with different sets of punches, so that a first set of punches impresses indentations into the tablets and the second set of punches, after filling, ensures a planar tablet surface by means of postcompression.

As described above, the tablets produced in accordance with the invention may be provided in whole or in part with a coating. Processes wherein the aftertreatment in step d) consists in applying a coating layer to the tablet area(s) in which the filled depression(s) is (are) located, or in applying a coating layer to the entire tablet, are preferred in accordance with the invention.

Following production, the laundry detergent and cleaning product tablets of the invention may be packed, the use of certain packaging systems having proven particularly useful since these packaging systems on the one hand increase the storage stability of the ingredients but on the other hand also, surprisingly, improve markedly the long-term adhesion of the depression filling. The present invention therefore additionally provides a combination of (a) laundry detergent and/or cleaning product tablet(s) of the invention and a packaging system containing the laundry detergent and/or cleaning product tablet(s), said packaging system having a moisture vapor

transmission rate of from 0.1 g/m^2/day to less than 20 g/m^2/day if said packaging system is stored at 23°C and a relative equilibrium humidity of 85%.

The packaging system of the combination of laundry detergent and cleaning product tablet(s) and packaging system has, in accordance with the invention, a moisture vapor transmission rate of from 0.1 g/m^2/day to less than 20 g/m^2/day when said packaging system is stored at 23°C and a relative equilibrium humidity of 85%. These temperature and humidity conditions are the test conditions specified in DIN Standard 53122, which allows minimal deviations (23 ± 1°C, 85 ± 2% relative humidity). The moisture vapor transmission rate of a given packaging system or material may be determined in accordance with further standard methods and is also described, for example, in ASTM Standard E-96-53T ("Test for measuring water vapor transmission of materials in sheet form") and in TAPPI Standard T464 m-45 ("Water vapor permeability of sheet materials at high temperature and humidity"). The measurement principle of common techniques is based on the water uptake of anhydrous calcium chloride which is stored in a container in the appropriate atmosphere, the container being closed at the top face with the material to be tested. From the surface area of the container closed with the material to be tested (permeation area), the weight gain of the calcium chloride, and the exposure time, the moisture vapor transmission rate may be calculated as follows:

$$MVTR = \frac{24 \cdot 10{,}000}{A} \cdot \frac{x}{y} \text{ [g / m}^2 \text{ / 24 h]}$$

where A is the area of the material to be tested in cm^2, x is the weight gain of the calcium chloride in g, and y is the exposure time in h.

The relative equilibrium humidity, often referred to as "relative atmospheric humidity", is 85% at 23°C when the moisture vapor transmission rate is measured in the context of the present invention. The ability of air to accommodate water vapor increases with temperature up to a particular maximum content, the so-called saturation content, and is specified in g/m^3. For example, 1 m^3 of air at 17° is saturated with 14.4 g of water vapor; at a temperature of 11°, saturation is reached with just 10 g of water vapor. The relative atmospheric humidity is the ratio, expressed as a percentage, of the actual water vapor content to the saturation content at the prevailing temperature. If, for example, air at 17° contains 12 g/m^3 water vapor, then the relative atmospheric humidity (RH) = (12/14.4)·100 = 83%. If this air is cooled, then saturation (100% RH) is reached at what is known as the dew point (in the example: 14°), i.e., on further cooling a precipitate is formed in the form of mist (dew). The humidity is determined quantitatively using hygrometers and psychrometers.

The relative equilibrium humidity of 85% at 23°C can be established precisely, for example, in laboratory chambers with humidity control, to +/-2% RH depending on the type of apparatus. In addition, constant and well-defined relative atmospheric humidities are formed in closed systems at a given temperature over saturated solutions of certain salts, these humidities deriving from the phase equilibrium between water partial pressure, saturated solution, and sediment.

The combinations of the invention, comprising laundry detergent and cleaning product tablets and packaging system, may of course in turn be packaged in secondary packaging, examples being cartons or trays, there being no need to impose further requirements on the secondary

packaging. The secondary packaging, accordingly, is possible but not necessary.

Packaging systems which are preferred in the context of the present invention have a moisture vapor transmission rate of from 0.5 $g/m^2/day$ to less than 15 $g/m^2/day$.

Depending on the embodiment of the invention, the packaging system of a combination of the invention contains one or more laundry detergent and cleaning product tablets. In accordance with the invention it is preferred either to design a tablet such that it comprises one application unit of the laundry detergent and cleaning product, and to package this tablet individually, or to pack into one packaging unit the number of tablets which totals one application unit. In the case of an intended dose of 80 g of laundry detergent and cleaning product, therefore, it is possible in accordance with the invention to produce and package individually one laundry detergent and cleaning product tablet weighing 80 g, but in accordance with the invention it is also possible to package two laundry detergent and cleaning product tablets each weighing 40 g into one pack in order to arrive at a combination in accordance with the invention. This principle can of course be extended, so that, in accordance with the invention, combinations may also comprise three, four, five or even more laundry detergent and cleaning product tablets in one packaging unit. Of course, two or more tablets in a pack may have different compositions. In this way it is possible to separate certain components spatially from one another in order, for example, to avoid stability problems.

The packaging system of the combination of the invention may consist of a very wide variety of

materials and may adopt any desired external forms. For reasons of economy and of greater ease of processing, however, preference is given to packaging systems in which the packaging material has a low weight, is easy to process, and is inexpensive. In combinations which are preferred in accordance with the invention, the packaging system consists of a bag or pouch of single-layer or laminated paper and/or polymer film.

The laundry detergent and cleaning product tablets may be filled unsorted, i.e. as a loose heap, into a pouch made of said materials. On esthetic grounds and for the purpose of sorting the combinations into secondary packaging, however, it is preferred to fill the laundry detergent and cleaning product tablets individually, or sorted into groups of two or more, into bags or pouches. For individual application units of the laundry detergent and cleaning product tablets which are located in a bag or pouch, a term which has become established in the art is that of the "flow pack". Flow packs of this kind may optionally then - again, preferably sorted - be packaged into outer packaging, which underscores the compact form of the tablet.

The single-layer or laminated paper or polymer film bags or pouches preferred for use as packaging systems may be designed in a very wide variety of ways: for example, as inflated pouches without a center seam or as pouches with a center seam which are sealed by means of heat, adhesives, or adhesive tapes. Single-layer pouch and bag materials include the known papers, which may if appropriate be impregnated, and also polymer films, which may if appropriate be coextruded. Polymer films that can be used as a packaging system in the context of the present invention are specified, for example, in *Hans Domininghaus, "Die Kunststoffe und ihre Eigenschaften", 3rd edition, VDI Verlag, Düsseldorf, 1988, page 193*. Figure 111 shown therein

also gives indications of the water vapor permeability of the materials mentioned.

Combinations which are particularly preferred in the context of the present invention comprise as packaging system a bag or pouch of single-layer or laminated polymer film having a thickness of from 10 to 200 μm, preferably from 20 to 100 μm, and in particular from 25 to 50 μm.

Although it is possible in addition to the abovementioned films and papers to use wax-coated papers in the form of cardboard packaging as a packaging system for the laundry detergent and cleaning product tablets, it is preferred in the context of the present invention for the packaging system not to comprise any cardboard boxes made of wax-coated paper. In the context of the present invention, the term "packaging system" always relates to the primary packaging of the tablets, i.e., to the packaging whose inner face is in direct contact with the tablet surface. No requirements whatsoever are imposed on any optional secondary packaging, so that all customary materials and systems can be used in this case.

As already mentioned earlier on above, the laundry detergent and cleaning product tablets of the combination of the invention comprise further ingredients of laundry detergents and cleaning products, in varying amounts, depending on their intended use. Independently of the intended use of the tablets, it is preferred in accordance with the invention for the laundry detergent and cleaning product tablet(s) to have a relative equilibrium humidity of less than 30% at 35°C.

The relative equilibrium humidity of the laundry detergent and cleaning product tablets may be

determined in accordance with common methods, the following procedure having been chosen in the context of the present investigations: a water-impermeable 1 liter vessel with a lid which has a closable opening for the introduction of samples was filled with a total of 300 g of laundry detergent and cleaning product tablets and held at a constant 23°C for 24 h in order to ensure a uniform temperature of vessel and substance. The water vapor pressure in the space above the tablets can then be determined using a hygrometer (Hygrotest 6100, Testoterm Limited, UK). The water vapor pressure is then measured every 10 minutes until two succeeding values show no deviation (equilibrium humidity). The abovementioned hygrometer permits direct display of the recorded values in % relative humidity.

Likewise preferred are embodiments of the combination of the invention wherein the packaging system is of resealable configuration. Combinations wherein the packaging system has a microperforation may also be realized advantageously in accordance with the invention.

What is claimed is:

1. A laundry detergent or cleaning product tablet comprising
   a) a compressed part (base tablet), which has at least one depression, and
   b) at least one further compressed part which is present impressed into said depression(s) in the base tablet.

2. The tablet as claimed in claim 1, wherein the weight ratio of base tablet to depression filling is within the range from 1:1 to 100:1.

3. The tablet as claimed in claim 2, wherein the weight ratio of base tablet to depression filling is within the range from 2:1 to 80:1.

4. The tablet as claimed in claim 3, wherein the weight ratio of base tablet to depression filling is within the range from 3:1 to 50:1.

5. The tablet as claimed in claim 4, wherein the weight ratio of base tablet to depression filling is within the range from 4:1 to 30:1.

6. The tablet as claimed in any one of claims 1 to 5, wherein the surface area of the impressed depression filling makes up from 1 to 25% of the total surface area of the filled tablet.

7. The tablet as claimed in claim 6, wherein the surface area of the impressed depression filling makes up from 2 to 20% of the total surface area of the filled tablet.

8. The tablet as claimed in claim 7, wherein the surface area of the impressed depression filling

makes up from 3 to 15% of the total surface area of the filled tablet.

9. The tablet as claimed in claim 8, wherein the surface area of the impressed depression filling makes up from 4 to 10% of the total surface area of the filled tablet.

10. The tablet as claimed in any one of claims 1 to 9, wherein the impressed depression filling dissolves more rapidly than the base tablet.

11. The tablet as claimed in any one of claims 1 to 10, wherein the impressed depression filling dissolves more slowly than the base tablet.

12. The tablet as claimed in any one of claims 1 to 11, wherein the base tablet has a density of more than 1000 g dm^{-3}.

13. The tablet as claimed in claim 12, wherein the base tablet has a density of more than 1025 g dm^{-3}.

14. The tablet as claimed in claim 13, wherein the base tablet has a density of more than 1050 g dm^{-3}.

15. The tablet as claimed in claim 14, wherein the base tablet has a density of more than 1100 g dm^{-3}.

16. The tablet as claimed in any one of claims 1 to 15, wherein the base tablet comprises builders in amounts of from 1 to 100% by weight based on the weight of the base tablet.

17. The tablet as claimed in claim 16, wherein the base tablet comprises builders in amounts of from 5 to 95% by weight.

18. The tablet as claimed in claim 17, wherein the base tablet comprises builders in amounts of from 10 to 90% by weight.

19. The tablet as claimed in claim 18, wherein the base tablet comprises builders in amounts of from 20 to 85% by weight.

20. The tablet as claimed in any one of claims 1 to 19, wherein the base tablet comprises phosphate(s).

21. The tablet as claimed in claim 20, wherein said phosphate(s) are alkali metal phosphate(s).

22. The tablet as claimed in claim 21, wherein said phosphate(s) are pentasodium or pentapotassium triphosphate (sodium or potassium tripolyphosphate).

23. The tablet as claimed in any one of claims 20 to 22, wherein said phosphate(s) are present in amounts of from 20 to 80% by weight based on the weight of the base tablet.

24. The tablet as claimed in claim 23, wherein said phosphate(s) are present in amounts of from 25 to 75% by weight.

25. The tablet as claimed in claim 24, wherein said phosphate(s) are present in amounts of 30 to 70% by weight.

26. The tablet as claimed in any one of claims 1 to 25, wherein the base tablet comprises carbonate(s) and/or hydrogen carbonate(s).

27. The tablet as claimed in claim 26, wherein said carbonate(s) is an alkali metal carbonate.

28. The tablet as claimed in claim 27, wherein said carbonate(s) is sodium carbonate.

29. The tablet as claimed in any one of claims 26 to 28, wherein said carbonate(s) is present in amounts of from 5 to 50% by weight based on the weight of the base tablet.

30. The tablet as claimed in claim 29, wherein said carbonate(s) is present in amounts of from 7.5 to 40% by weight.

31. The tablet as claimed in claim 30, wherein said carbonate(s) is present in amounts of from 10 to 30% by weight.

32. The tablet as claimed in any one of claims 1 to 31, wherein the base tablet comprises silicate(s).

33. The tablet as claimed in claim 32, wherein said silicate(s) is an alkali metal silicate.

34. The tablet as claimed in claim 33, wherein said silicate(s) is crystalline or amorphous alkali metal disilicate(s).

35. The tablet as claimed in any one of claims 32 to 34, wherein said silicate(s) is present in amounts of from 10 to 60% by weight based on the weight of the base tablet.

36. The tablet as claimed in claim 35, wherein said silicate(s) is present in amounts of from 15 to 50% by weight.

37. The tablet as claimed in claim 36, wherein said silicate(s) is present in amounts of from 20 to 40% by weight.

38. The tablet as claimed in any one of claims 1 to 37, wherein the base tablet has total surfactant contents of less than 5% by weight based on the weight of the base tablet.

39. The tablet as claimed in claim 38, wherein the base tablet has total surfactant contents of less than 4% by weight.

40. The tablet as claimed in claim 39, wherein the base tablet has total surfactant contents of less than 3% by weight.

41. The tablet as claimed in claim 40, wherein the base tablet has total surfactant contents of less than 2% by weight.

42. The tablet as claimed in any one of claims 1 to 41, wherein the base tablet comprises bleaches selected from the group consisting of oxygen or halogen bleaches.

43. The tablet as claimed in claim 42, wherein said bleaches are chlorine bleaches.

44. The tablet as claimed in claim 43, wherein said bleaches are sodium perborate and sodium percarbonate.

45. The tablet as claimed in any one of claims 42 to 44, wherein said bleaches are present in amounts of from 2 to 25% by weight based on the weight of the base tablet.

46. The tablet as claimed in claim 45, wherein said bleaches are present in amounts of from 5 to 20% by weight.

47. The tablet as claimed in claim 46, wherein said bleaches are present in amounts of from 10 to 15% by weight.

48. The tablet as claimed in any one of claims 1 to 47, wherein the base tablet comprises bleach activators selected from the groups consisting of polyacylated alkylenediamines, N-acyl imides, acylated phenolsulfonates and N-methylmorpholiniumacetonitrile methyl sulfate (MMA).

49. The tablet as claimed in claim 48, wherein said polyacylated alkylenediamine is tetraacetyl-ethylenediamine (TAED).

50. The tablet as claimed in claim 48, wherein said imide is N-nonanoylsuccinimide (NOSI).

51. The tablet as claimed in claim 48, wherein said phenolsulfonate is n-nonanoyl- or isononanoyloxy-benzenesulfonate (n- or iso-NOBS).

52. The tablet as claimed in any one of claims 48 to 51, wherein said bleach activators are present in amounts of from 0.25 to 15% by weight based on the weight of the base tablet.

53. The tablet as claimed in claim 52, wherein said bleach activators are present in amounts of from 0.5 to 10% by weight.

54. The tablet as claimed in claim 53, wherein said bleach activators are present in amounts of from 1 to 5% by weight.

55. The tablet as claimed in any one of claims 1 to 54, wherein the base tablet comprises silver protectants selected from the group consisting of triazoles, benzotriazoles, bisbenzotriazoles, aminotriazoles, alkylaminotriazoles and the transition metal salts or transition metal complexes.

56. The tablet as claimed in claim 55, wherein said silver protectant is benzotriazole and/or alkylaminotriazole.

57. The tablet as claimed in either of claims 55 or 56, wherein said silver protectant is present in amounts of from 0.01 to 5% by weight based on the weight of the base tablet.

58. The tablet as claimed in claim 57, wherein said silver protectant is present in amounts of from 0.05 to 4% by weight.

59. The tablet as claimed in claim 58, wherein said silver protectant is present in amounts of from 0.5 to 3% by weight.

60. The tablet as claimed in any one of claims 1 to 59, wherein the base tablet further comprises one or more substances selected from the groups consisting of enzymes, corrosion inhibitors, scale inhibitors, cobuilders, dyes and/or fragrances.

61. The tablet as claimed in claim 60, comprising said substances in total amounts of from 6 to 30% by weight based on the weight of the base tablet.

62. The tablet as claimed in claim 61, comprising said substances in amounts of from 7.5 to 25% by weight.

63. The tablet as claimed in claim 62, comprising said substances in amounts of from 10 to 20% by weight.

64. The tablet as claimed in any one of claims 1 to 63, wherein the part impressed into the base tablet comprises at least one active substance selected from the group consisting of enzymes, surfactants, soil release polymers, disintegration aids, bleaches, bleach activators, bleaching catalysts, silver protectants and mixtures thereof.

65. The tablet as claimed in any one of claims 1 to 64, wherein the base tablet or the part impressed into the base tablet comprises bleaches while the other part comprises bleach activators.

66. The tablet as claimed in any one of claims 1 to 65, wherein the base tablet or the part impressed into the base tablet comprises bleaches while the other part comprises enzymes.

67. The tablet as claimed in any one of claims 1 to 66, wherein the base tablet or the part impressed into the base tablet comprises bleaches while the other part comprises corrosion inhibitors.

68. The tablet as claimed in any one of claims 1 to 68, wherein the base tablet or the part impressed into the base tablet comprises bleaches while the other part comprises surfactants.

69. The tablet as claimed in claim 68, wherein said surfactants are nonionic surfactants.

70. The tablet as claimed in claim 69, wherein said surfactants are alkoxylated alcohols having 10 to 24 carbon atoms and from 1 to 5 alkylene oxide units.

71. The tablet as claimed in any one of claims 1 to 70, wherein the base tablet and the part impressed into the base tablet comprise the same active substance in different amounts.

72. The tablet as claimed in any one of claims 1 to 71, wherein the particles impressed into the base tablet consist of

a) from 30 to 90% by weight of one or more carrier materials,

b) from 5 to 40% by weight of one or more coating substances having a melting point of more than 30°C,

c) from 5 to 40% by weight of one or more active substances, and

d) from 0 to 10% by weight of further active and auxiliary substances.

73. The tablet as claimed in claim 72, wherein paraffin(s) or polyalkylene glycols are present in the particles as coating substance.

74. The tablet as claimed in either of claims 72 and 73, wherein the particles impressed into the base tablet comprise, as active substances, nonionic surfactant(s) and/or bleaches and/or bleach activators and/or enzyme(s) and/or corrosion inhibitors and/or fragrances.

75. The tablet as claimed in any one of claims 1 to 71, wherein the particles impressed into the base tablet consist of

a) from 40 to 99.5% by weight of one or more coating substances having a melting point of more than 30°C,

b) from 0.5 to 60% by weight of one or more liquid enzyme preparations dispersed in the coating substance(s), and

c) from 0 to 20% by weight of further carrier materials, auxiliary substances and/or active substances.

76. The tablet as claimed in claim 75, wherein the particles consist of from 50 to 97.5% by weight of one or more coating substances having a melting point of more than 30°C.

77. The tablet as claimed in claim 76, wherein the particles consist of from 60 to 95% by weight of one or more coating substances having a melting point of more than 30°C.

78. The tablet as claimed in claim 77, wherein the particles consist of from 70 to 90% by weight of one or more coating substances having a melting point of more than 30°C.

79. The tablet as claimed in any one of claims 75 to 78, wherein said particles contain from 1 to 40% by weight of one or more liquid enzyme preparations dispersed in the coating substance(s).

80. The tablet as claimed in claim 79, wherein said particles contain from 2.5 to 30% by weight of one or more liquid enzyme preparations dispersed in the coating substance(s).

81. The tablet as claimed in claim 80, wherein said particles contain from 5 to 25% by weight of one or more liquid enzyme preparations dispersed in the coating substance(s).

82. The tablet as claimed in any one of claims 75 to 81, wherein said particles contain from 0 to 15% by weight of further carrier materials, auxiliary substances and/or active substances.

83. The tablet as claimed in claim 82, wherein said particles contain from 0 to 10% by weight of further carrier materials, auxiliary substances and/or active substances.

84. The tablet as claimed in claim 82, wherein said particles contain from 0 to 5% by weight of further carrier materials, auxiliary substances and/or active substances.

85. The tablet as claimed in any one of claims 1 to 84, which comprises less than 2% by weight of free water.

86. The tablet as claimed in claim 85, which comprises less than 1.5% by weight of free water.

87. The tablet as claimed in claim 86, which comprises less than 1% by weight of free water.

88. The tablet as claimed in 87, which comprises less than 0.5% by weight of free water.

89. The tablet as claimed in any one of claims 1 to 88, wherein the part impressed into the base tablet is covered with a coating layer.

90. The tablet as claimed in any one of claims 1 to 89, wherein the pH of a 1% strength solution of the base tablet in water is in the range of from 8 to 12.

91. The tablet as claimed in claim 90, wherein the pH of a 1% strength solution of the base tablet in water is in the range of from 9 to 11.

92. The tablet as claimed in claim 91, wherein the pH of a 1% strength solution of the base tablet in water is in the range of from 9.5 to 10.

93. The tablet as claimed in any one of claims 1 to 92, wherein the pH of a 1% strength solution of the entire tablet in water is in the range of from 7 to 11.

94. The tablet as claimed in claim 93, wherein the pH of a 1% strength solution of the entire tablet in water is in the range of from 7.5 to 10.

95. The tablet as claimed in claim 94, wherein the pH of a 1% strength solution of the entire tablet in water is in the range of from 8 to 9.5.

96. A process for producing laundry detergent and cleaning product tablets, which comprises the steps of

a) compressing a particulate premix to form a compressed part (base tablet) which has at least one depression,

b) filling one or more particulate compositions into said depression(s),

c) compressing the composition(s) filled in in step b) to form (a) further compressed part(s) which is/are present in impressed form in said depression(s) of the base tablet, and

d) optionally aftertreating individual tablet areas or the entire tablet.

97. The process as claimed in claim 96, wherein the particulate premix in step a) has a bulk density of at least 500 g/l.

98. The process as claimed in claim 97, wherein the particulate premix in step a) has a bulk density of at least 600 g/l.

99. The process as claimed in claim 98, wherein the particulate premix in step a) has a bulk density of at least 700 g/l.

100. The process as claimed in any one of claims 96 to 99, wherein the particulate premix in step a) has particle sizes of between 100 and 2000 μm.

101. The process as claimed in claim 100, wherein the particulate premix in step a) has particle sizes of between 200 and 1800 μm.

102. The process as claimed in claim 101, wherein the particulate premix in step a) has particle sizes of between 400 and 1600 μm.

103. The process as claimed in claim 102, wherein the particulate premix in step a) has particle sizes of between 600 and 1400 μm.

104. The process as claimed in any one of claims 96 to 103, wherein the particulate composition(s) in step b) has/have a bulk density of at least 500 g/l.

105. The process as claimed in claim 104, wherein the particulate composition(s) in step b) has/have a bulk density of at least 600 g/l.

106. The process as claimed in claim 105, wherein the particulate composition(s) in step b) has/have a bulk density of at least 700 g/l.

107. The process as claimed in any one of claims 96 to 106, wherein the particulate composition(s) in step b) has/have particle sizes of between 100 and 2000 μm.

108. The process as claimed in claim 107, wherein the particulate composition(s) in step b) has/have particle sizes of between 200 and 1800 μm.

109. The process as claimed in claim 108, wherein the particulate composition(s) in step b) has/have particle sizes of between 400 and 1600 μm.

110. The process as claimed in claim 109, wherein the particulate composition(s) in step b) has/have particle sizes of between 600 and 1400 μm.

111. The process as claimed in any one of claims 96 to 110, wherein compression in step c) takes place at compressive pressures of from 0.01 to 50 kN cm^{-2}.

112. The process as claimed in claim 111, wherein compression in step c) takes place at compressive pressures of from 0.1 to 40 kN cm^{-2}.

113. The process as claimed in claim 112, wherein compression in step c) takes place at compressive pressures of from 1 to 25 kN cm^{-2}.

114. The process as claimed in any one of claims 96 to 113, wherein compression in step c) takes place at compressive pressures of from 1 to 100 kN cm^{-2}.

115. The process as claimed in claim 114, wherein compression in step c) takes place at compressive pressures of from 2.5 to 50 kN cm^{-2}.

116. The process as claimed in claim 115, wherein compression in step c) takes place at compressive pressures of from 5 to 25 kN cm^{-2}.

117. The process as claimed in any one of claims 96 to 116, wherein the aftertreatment in step d) consists in applying a coating layer to the tablet area(s) in which the filled depression(s) is(are) located.

118. The process as claimed in any one of claims 96 to 117, wherein the aftertreatment in step d) consists in applying a coating layer to the entire tablet.

119. A combination comprising (a) laundry detergent and/or cleaning product tablet(s) as claimed in any one of claims 1 to 95 and a packaging system containing the laundry detergent and/or cleaning product tablets, wherein said packaging system has a moisture vapor transmission rate of from 0.1 $g/m^2/day$ to less than 20 $g/m^2/day$ if said packaging system is stored at 23°C and a relative equilibrium humidity of 85%.

120. The combination as claimed in claim 119, wherein said packaging system has a moisture vapor transmission rate of from 0.5 $g/m^2/day$ to less than 15 $g/m^2/day$.

121. The combination as claimed in either of claims 119 or 120, wherein the laundry detergent and/or cleaning product tablet(s) has/have a relative equilibrium humidity of less than 30% at 35°C.

122. The combination as claimed in any one of claims 119 to 121, wherein said packaging system consists of a bag or pouch of single-layer or laminated paper and/or polymer film.

123. The combination as claimed in claim 122, wherein said packaging system consists of a bag or pouch of single-layer or laminated polymer film having a thickness of from 10 to 200 μm.

124. The combination as claimed in claim 123, wherein said packaging system consists of a bag or pouch of single-layer or laminated polymer film having a thickness of from 20 to 100 μm.

125. The combination of claim 124, wherein said packaging system consists of a bag or pouch of single-layer or laminated polymer film having a thickness of from 25 to 50 μm.

126. The combination as claimed in any one of claims 119 to 125, wherein said packaging system does not comprise any cardboard boxes made of wax-coated paper.

127. The combination as claimed in any one of claims 119 to 126, wherein said packaging system is of resealable configuration.

128. The combination as claimed in any one of claims 119 to 127, wherein said packaging system has a microperforation.